Green Chemistry and Sustainable Technology

Alberto Figoli
Alessandra Criscuoli *Editors*

Sustainable Membrane Technology for Water and Wastewater Treatment

Springer

Green Chemistry and Sustainable Technology

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Preface

Membrane operations find application in all industrial sectors and have been proved to well compete with conventional production/separation systems. There are already different fields that successfully adopt membrane units, like dialysis, sea and brackish water desalination, and municipal wastewater treatment. However, the need for a sustainable development has imposed new targets to be reached in near future, such as a reduced use of energy and raw materials and lower admissible limits for contaminants discharged into the environment. In this context, the aim of the book is to analyze the sustainability of membrane operations applied at industrial scale, as well as that of those under investigation at lab/pilot scale. It covers not only technical and environmental issues in membrane technology but also economic, regulatory and policy aspects, addressing the challenges for future research in membrane field. The first few chapters of the book deal with sustainability indicators, Life Cycle Assessment (LCA), and process intensification applied to membrane operations. Then, the preparation step of both polymeric and inorganic membranes is presented and discussed, stressing on the possibility of using more sustainable materials, solvents, and processes in the membrane fabrication. As industrial membrane operations, reverse osmosis in desalination, membrane bioreactors for municipal wastewater treatment, and pressure-driven wastewater treatment in agrofood and textile industries are analyzed from a sustainable point of view. Concerning the membrane processes still at a lab/pilot scale, the analysis is made for the: (i) recovery of valuable compounds from wastewater streams, (ii) removal of toxic compounds from water/wastewater, (iii) approaching the zero liquid discharge in desalination.

The book was prepared by leading international researchers (membranologists) having extensive experiences in water and wastewater treatment. We would like to express them our sincere thanks for their contribution and support. We are also very grateful to Prof. Pietro Tundo at Università di Venezia who gave us the possibility of making this book within the series "Green Chemistry and Sustainable

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Chapter 1
Sustainability and How Membrane Technologies in Water Treatment Can Be a Contributor

Subhas K. Sikdar and Alessandra Criscuoli

Abstract Water treatment technologies inherit the environmental, economic, and societal burdens either from polluted natural sources for potable water, or from domestic sewer water for municipal wastewater treatment plants, or from various industrial processing plants that produce highly contaminated wastewater. Application of various membrane technologies for wastewater has been growing because they enjoy relative advantage over other technologies in terms of sustainability. This advantage mainly emanates from economic benefits, ease of operation and safety. This chapter discusses what sustainability means for wastewater treatment and what specific sustainability advantages membrane processes can demonstrate. Applicable sustainability indicators are identified for various membrane technologies that can tackle a large number of wastewater problems.

Keywords Sustainability indicators · Sustainability assessment · Membrane technologies · Wastewater treatment

1.1 Introduction

Mobile and immobile biological organisms have evolved through millennia to become highly complex and resilient, performing many elaborate vital tasks throughout their life cycles without failing. When we think of what keep them alive and functioning, we cannot but conclude that these biological factories are a very complex network that works in amazing harmony to process input ingredients, called nutrients, to provide growth of constituent cells and reject waste products on

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a continual basis. Cell membranes, which are in every cell of the living systems, carry out an enormous amount of transfers of molecules and ions across vital organs and all individual cells. Cell membranes act both as semipermeable barriers and gatekeepers, allowing certain molecules to go through, blocking other molecules in their track. Constitutionally they are made of glycerophospholipids with specific proteins embedded in them. Functionally they play all the parts industrial membranes also can be designed to play. Such parts can be osmosis, microfiltration, nanofiltration, and facilitated transport. All kinds of dissimilar molecules such as sugars, other neutral molecules, ions, lipids, and proteins can be preferentially transported or blocked depending on the design of biological membranes. When the organisms become sick or they die, the reasons can be traced to some malfunctions in these transfers. Nature developed membranes to carry out these vital transfers because they are extremely efficient. Membranes surely do not define the organisms, but they should be credited for facilitating their proper designed functions. Membranes make the living systems sustainable. The common meaning of sustainability thus is intimately connected to natural membrane operations. Since the major constituent of living bodies is water, these amazing natural membranes function efficiently in aqueous environment. It is instructive to keep natural membranes and their functions in mind when we develop industrial membranes for drinking water production or wastewater treatment applications.

Biological membranes provide many more specialized functions than we would ever encounter in water systems, where the predominant outcome is preferential transport of water from sources that can be as varied as groundwater, river water, lake water, brackish water, seawater, and municipal or industrial wastewater. The barrier role is simply to let water go through, blocking everything else. Rivers, lakes, and underground aquifers have been the main sources of water for human consumption, especially in metropolitan areas. River water is usually muddy and replete with microbes. The need to purify it for human consumption led to filtration using sands and disinfection using chlorine. Groundwater often can be directly used without disinfection because the Earth's crust does a fine job at removing particulates as well as microbes. Nevertheless, in some areas, inorganic dissolved impurities such as arsenic can and do create health issues [1–3]. In arid areas, as in the Middle East, water is scarce and people have resorted to thermal techniques such as multi-effect evaporators or distillation for obtaining safe drinking water from seawater. The invention of the reverse osmosis provided a cheaper alternative to distillation, because all thermal methods are energy intensive and therefore expensive. They also generate pollution.

Membrane technologies are deemed to be low-energy separation processes and operated under ambient conditions. Membranes will play an increasing role for water purification and recovery systems because safe water is in increasing demand resulting from increasing population, improving living standards assisted by sanitation needs and increased industrial outputs to support a larger population. Membrane operations are not cheap, however. The membranes themselves are a major cost item, and reverse osmosis (RO) operating at high pressures[1] can be a significant pumping cost. Membranes are prone to fouling and require protection for continuous operation. Nevertheless, the research efforts made in last years on membrane materials and module development as well as on the integration of different membrane units led to a significant improvement of the membranes efficiency and stability in long-term applications.

1.2 Water Types

Water treatment roughly has three purposes:

a. **Producing water from municipal sewer treatment plants for discharge**. Here the water that goes into these plants has biosolids, particulates, and a tremendous amount of microbial organisms. Because of compliance needs of cleaning this sewer water to a level that can be safely discharged into a receiving stream, such as a river, the main goal is to remove the solid matter, toxic heavy metals, and disinfect the effluents for pathogens before discharging. Industrial wastewater similarly has to comply with regulations requiring the removal of all kinds of toxic organics and heavy metals from them. In the case of industrial wastewater generally, biological treatment is used for the treatment of the organics, and physical/chemical methods for the removal of heavy metals. In the case of municipal sewer water the desired method is activated sludge process in which naturally occurring microorganisms destroy the organic matter producing clear water and a residue known as biosolids. These biosolids will in general have pathogens and heavy metals in them. Returning the biosolids for use as soil amendments does require some disinfection. The membrane alternative successfully developed and applied in recent times is the Membrane Bioreactor (MBR) where the action of microorganisms is coupled with that of microfiltration (MF)/ultrafiltration (UF) membranes. A primer published by US EPA is a good source for information on all of these issues [4].
b. **Producing industrial water for in-plant or in-process recycling**. Because of the immense diversity of industrial wastewater depending on the nature of the industry, there cannot be a generic method applicable to all industrial wastewaters. The quality requirement for these recycle waters depends on the type of reuse and will determine the specific process to be applied for the treatment. For instance, for cooling water, say in a power plant, prevention of inorganic scale formation is the dominant concern. For recycling ultrapure water for semiconductor processing, even a tiny concentration of silica or bacteria could be very damaging. Stringent purification methods are needed for such recycling. Technologies such as precipitation, evaporation/distillation, absorption or

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[1] The required pressure for brakish water can be as high as 26 bar, and for seawater as high as 80 bar.

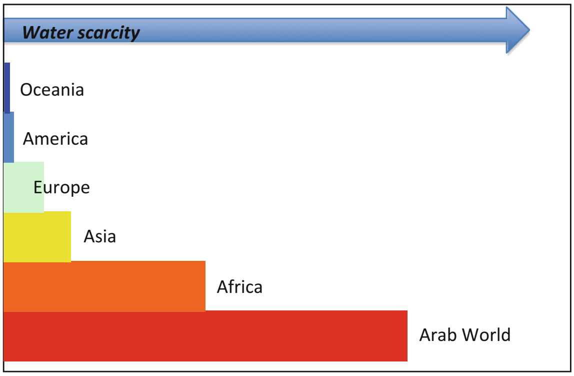
adsorption, solvent extraction, and crystallization can be among the choices [5, 6]. Membrane processes are also an option to be considered, especially after the development of membrane contactors that are able to implement gas–liquid operations, liquid–liquid extractions, and distillation.

c. **Producing drinking water**. Typically the source for this purpose is slightly saline lake or river water, or groundwater. Disinfection is always used because the human consumption is the objective for such waters. For more than a century, this objective has been served by established technologies, such as sand filtration followed by disinfection with chlorine or ozone. Lately because of toxic effects of disinfection by-products resulting from chlorination, some municipalities are moving away from chlorine and are beginning to adopt the use of chloramines. Ozonation is also an alternative to chlorine. Adsorption beds with granular activated carbon, though not used universally yet for cost reasons, is an effective way to polish the drinking water before distribution to customers. Membranes can also find interesting applications in this field. Brackish or seawater is particularly interesting for water-stressed areas. In some countries of the Middle East, drinking water is produced by evaporation or distillation. As mentioned earlier this is a costly option. The other option is reverse osmosis (RO), and this option is growing. Israel operates several large reverse osmosis plants on the Mediterranean coast and has been supplying affordable drinking water to its industry and citizens for sometime. Interest in RO around the world is growing as freshwater progressively becomes less and less available.

1.3 Sustainability Concern

So why is the concept of sustainability relevant to the treatment of water? To answer this question, we have to introduce the idea of sustainability and attempt to show a link to water treatment. At the outset, we have to acknowledge the fact that almost no one in water treatment business at present is concerned with sustainability. This is simply because predominantly sustainability concerns are driven by the environmental impacts of anthropogenic pollution released to air, water, and soil, causing depletion of natural resources and adverse health impacts on society and ecology. Per se, water treatment does not cause these impacts; actually it is a means to remove such impacts from municipal wastewaters and from our other activities such as manufacturing operations, energy production facilities, and the products we use, consume, and dispose. However, there are many naturally water-stressed areas on earth; others are becoming water-stressed as a consequence of freshwater withdrawal from aquifers at a higher rate than nature can recharge. Overall, 159 countries in the world suffer from water stress and the “top 5” are Egypt, Kuwait, United Arab Emirates, Libya, and Saudi Arabia [7]. In Fig. 1.1, the water scarcity by region is summarized on the basis of the data reported by [8] and [9].

Fig. 1.1 The water scarcity by region II



There is also the fear that climate change might alter water availability conditions pushing some areas into water-stressed category.[2] At the regional geographical scale the concern is clearly valid, and measures are warranted to protect people from catastrophic consequences. Apart from availability issues (water quantity), there is also polluted waterbodies, such as rivers, lakes, and groundwater in many parts of the world (water quality). Thus water quality is also a sustainability concern. Water treatment is a solution to these water sustainability concerns. At the regional and global scales, these problems are related to water resources, implying a mismatch between demand and supply. Water treatment technologies and public policy are the primary means of tackling such resource sustainability issues.

As we will see shortly, sustainability, in essence, is relative. This relativity aspect is more meaningful when we focus on treatment technologies. This is important because we can do something about it now, as against the climate change affecting regional water sustainability, the latter being beset with uncertainties and not under control of water technologists. There can be various technology schemes for treating water for the three goals of Sect. 1.2. When we compare competing technologies, we would be forced to look at the environmental impacts of these technologies. Treatment technologies are processes and they have inputs and outputs. Inputs will include material (such as sorbents, membranes, or evaporators), chemicals, and energy. Outputs are the water of desired quality either for consumption, recycle, or discharge, and wastes such as sludge or residues. All emissions to air coming from the water treatment facilities are also outputs. The use of the input material and having to deal with the outputs will have environmental impacts, however small. Our stewardship responsibility is to use the technology that has the least environmental impact. That is why we will have to compare the relative sustainability of the competing technologies.

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[2] According to the Intergovernmental Panel for Climate Change, climate change will affect the hydrological cycles of the earth, making some areas arid, others wetter [10].

There is another factor that is relevant to sustainability: cost of technologies. From the sustainability viewpoint, the goal of the technology adopters will have to be to accept the technology that has the least environmental and societal impact they can afford.

1.4 Concept of Sustainability and Its Relevance to Treatment Technologies

It is generally assumed that our profligate use of limited natural resources is causing widespread environmental degradation, creating social inequity in the present generation and threatening not to leave enough resources for the future generations. Paraphrasing the definition given by the Brundtland Commission [11] sustainable development is industrial development done with restrained use of natural resources (materials, energy, water) so that the current generation can satisfy its needs, yet not deprive the future generations of their ability to satisfy their own needs to attain their desired living standards. In each case, the needs have to be satisfied without harming the environment that sustains human and ecological health. This objective requires measuring quantitatively those environmental impacts that can result from anthropogenic activities, both municipal and industrial.

Sustainability can be illustrated by three intersecting domains of a Venn diagram, each domain representing either societal, environmental, or economic, as shown in Fig. 1.2.

To ascertain the relative superiority of a technology from sustainability viewpoint, we need to quantitatively assess the impacts on the three domains of Fig. 1.2 of the competing treatment technologies for the targeted purpose. For this purpose, **sustainability assessment is essentially an accounting of what the system is doing to itself and to the surrounding in terms of environmental, societal, and economic impacts, and how these impacts can be minimized**.

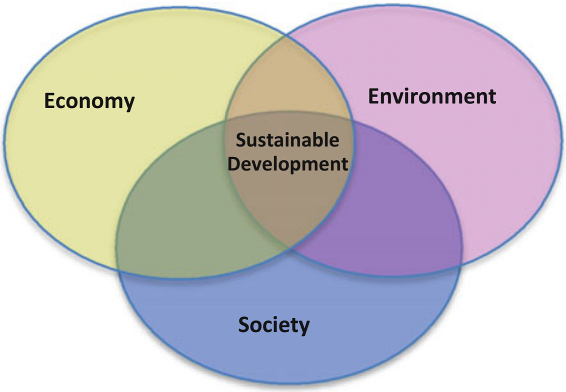

Fig. 1.2 Sustainability happens at the intersection of the three domains

We need indicators for making sustainability assessment. Indicators are factors that indicate an aspect of impact on one or more of these three domains.

1.4.1 Indicators (or Metrics) for Water Treatment Businesses

The indicators used for business systems generally represent a list of key principles:

- **Energy** use from fossil sources should be minimized, and, to the extent possible, should be shifted to renewable energy
- **Materials** that are nonrenewable should also be minimized, and attempts should be made to replace them with renewable or recycled materials
- **Toxics Release** to the environment, which is regulated in developed nations, should be minimized. Ideally, operating beyond compliance with regulations is a good goal.
- **Wastes** creation should be minimized and where unavoidable, discharges to the environment should aim for "beyond compliance" achievement. Of particular importance is the release of global warming **greenhouse gases (GHG)** which should be continually decreased. Release of stratospheric **ozone-depleting** substances should be minimized, and wherever possible, its use eliminated.
- **Cost** of treatment should be minimized with technical innovations.
- **Worker safety** in the work environment should be of paramount importance.
- **Adverse Societal** impact should be addressed and scrupulously avoided.
- Indicators should incorporate **life cycle** thinking for all ingredients used in treatment. Economic, environmental, and societal impacts of material, energy, and labor inputs into created products together with the impacts from product in its use, disposal, and waste phases should be evaluated and reduced [12].

At the level of water treatment technologies, the following indicators can be suggested, as shown in Table 1.1. The indicator classification is also shown in parentheses. The descriptors within parentheses for the indicators show the type of indicators as per Fig. 1.2.

1.4.2 Sustainability Assessment

The sustainability assessment can be made following the steps reported below.

a. The first task in sustainability assessment is to define the system that would be subjected to this analysis. Depending on the situation at hand, it could simply be the plant that treats the water, be it municipal or industrial wastewater or a drinking water works. If the treatment plant is the defined system, we would consider the surrounding as the space outside the plant. We would have to

Table 1.1 Suggested indicators for water treatment technologies

Water indicator	Remarks
Cost intensity (economic)	How much does it cost to treat 1000 gallons of feed water
Nonrenewable energy intensity (sustainable)	Megajoules of fossil or nuclear energy needed to treat 1000 gallons of feed water
Renewable energy intensity (sustainable)	Megajoules of renewable energy, such as hydro, biomass, wind used per 1000 gallons of feed water
Greenhouse gas emission (environmental)	kg of GHG from all sources released to treat 1000 gallons of feed water
Waste intensity (environmental)	kg of solid waste or gallons of water waste created from technology per 1000 gallons of feed water
Cost of waste treatment (economic)	$ per waste from 1000 gallons of feed water
Chemicals intensity (economic)	$ of chemicals to treat 1000 gallons of feed water
Investment cost (economic)	$ of investment for a scale at which the installation is profitable or socially acceptable
Toxics released treated (sustainable)	kg of toxics released to the environment per 1000 gallons of water
Value of recoverables (sustainable)	$ of value recovered per 1000 gallons of feed water

assume that the designed treatment plant is efficient enough to produce the effluent to meet water quality standards that are set by the authorities, and the treated residuals are benign enough to either represent an economic value or are of small financial liability when disposed. In most cases, these are reasonable assumptions to make.

b. At this point we need to identify the indicators to be used to characterize the system. Supposing that the suggested indicators of Table 1.1 are accepted, data on the indicators need to be collected and or calculated in the proper units.
c. We need to show that the set of indicator values of this plant practicing one specific technology can be compared with a very similar plant that practices or is proposed to practice another technology for treatment.

   Most of these indicator valuations are straightforward to calculate from the facility's data inventory. There are various tools available in the marketplace to compute the environmental impacts of the toxics released to the environment from the plant.[3] If necessary, the process can be optimized against the indicators

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[3] Software packages such as Simapro (http://simapro.com/business/?gclid=CLPpo834rcgCFdCPHwodTnQPQw), Gabi (http://www.gabi-software.com/america/index/) can be used. These packages provide various environmentally relevant impacts (such as acidification potential, ozone depletion potential, cancer causing potential, etc.) per unit mass of the toxics released. USA EPA has freely available package, TRACI, which also can be used for impact assessment.

using process optimization tools.[4] The objective of the optimization should be to find operating conditions under which the sustainability objective can be met, i.e., to find an affordable process that satisfies or goes beyond all applicable regulations and standards.

d. Having collected the indicator data for the specific technology, we need similar data set for another technology, so that we can compare the data sets to see which one is superior, i.e., more sustainable. The comparison can be made in one of the two ways. We discuss that in the next section.

1.5 Comparative Sustainability

There are two main methods that can be used for making the comparison:

a. The first method of comparison is to show each data set on a spider (or radar) diagram, appropriately scaled so that the comparison can be done easily by inspection. The data will look like this (Fig. 1.3).
This representation shows how the data sets look for the two processes we want to compare. We have plotted the values of the ten indicators on the polygon, where each apex represents the maximum value of an indicator. Supposing we scaled the data properly to indicate that the maximum is the worst possible performance of that indicator, then smaller number is better for each indicator. This directionality is important. If the original data are not in line with this notion, the data can be easily transformed to a derived indicator that does satisfy this directionality condition. The inference we make about the superiority of one process over another is not straightforward with this approach. This is because some of the indicators are better in one process, other worse. Picking one as the superior requires a subjective value judgement.
b. The second method is to create an aggregate index of the ten indicators. We will suggest one based on the Euclidean distance of the process index from an ideal process which will be better than either of the processes [13, 14]. The computation of the Euclidean distance D is shown in Eq. 1.1 [13]. There are other aggregates one can use, such as the Mahalonobis distance [15] and Canberra distance [16] for the same purpose. It has been shown by Ref. [15] that all these methods provide the same results with varying degrees of robustness.

$$D_e = \sqrt{\sum_{j}^{n} \left| c_j \frac{\left(x_j - x_{j0}\right)}{\left(x_j - x_{j0}\right)_{max}} \right|^2} \tag{1.1}$$

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[4] Such as Aspen Plus (http://www.aspentech.com/products/engineering/aspen-plus/).

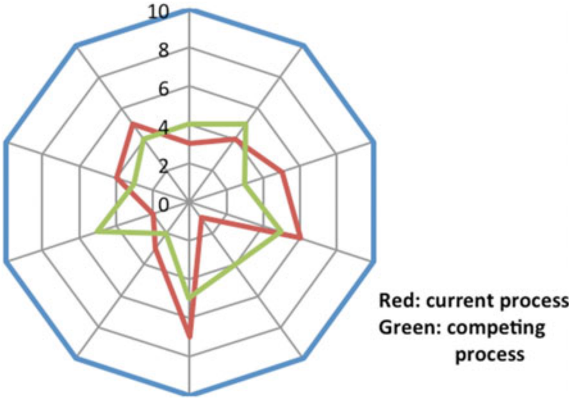

Fig. 1.3 Spider diagram for comparing indicator values

Suppose we have a membrane process, X_1 which needs to be compared with an alternative process (membrane or non-membrane process) X_2 for their relative sustainability performances. We need to establish a synthetic reference process $X_{0,}$ and we want to use n number of indicators to do the comparison. We have collected the indicator data for the two actual processes. The synthetic process X_0 can be constructed by collecting the minimum values of the indicators from the two data sets. The principle of directionality mandates that we define the indicators in such as a way that higher numbers are less desirable than the lower numbers. Thus we have three data sets representing the processes, $X_{1,}$ X_2, and X_0. Equation 1.1 shows the formula for the Euclidean distance between any of the two processes from the reference process. Since we chose the indicator data for the reference process as the best achievable between the two contenders, the equation tells us how far the two processes exist from the reference process. The process that is closer to X_0 will have the better sustainability performance. By calculating the Euclidean distance we have essentially aggregated the indicators in a single index to represent the sustainability performance of the processes. In Eq. 1.1, x_j is the value of the jth indicator and x_{j0} is the corresponding indicator value of the synthetic process. The difference of the indicator values is normalized by the maximum difference for that indicator in the data sets. This normalization makes the ratio dimensionless, making it easier to do the calculation without worrying about different units that the indicators carry with them. The term c_j is called a weighting factor to account for the relative importance of the indicators based on experience. This term can be viewed as the weighting that society imparts on the indicators. The default value of the weighting is 1 for all indicators, signifying that we have insufficient information to judge the weighting. For membrane processes, this default value is easily defensible. The Euclidean distance is an easy way to compare the processes and make inference about the relative sustainability performances, in contrast to the spider diagram method outlined before. Though we illustrated the concept with only two contender processes, the concept is valid for any number of processes, as long the processes are similar, i.e., it is worth comparing them and that they share the same number of indicators that fully characterize them.

1.6 Sustainability of Membrane Processes

Of the membrane processes in water treatment, the ones we are most likely to encounter are reverse osmosis, nanofiltration (NF), ultrafiltration, microfiltration, more recently also MBR and perhaps membrane distillation (MD) in the future. The most important factors that will characterize the processes from a sustainability viewpoint are cost of operation, energy use, separation efficiency, and the residuals. These factors have been expressed as indicators with enhanced granularity in the suggested indicator table. In what follows, the various membrane processes that are important to the treatment of water are presented. In the concluding remarks, the relevance of sustainability of these membrane processes will be discussed.

1.6.1 Pressure-Driven Membrane Operations

In pressure-driven membrane operations, a pressure is usually applied to the feed stream, in order to promote the separation through the membrane. One side of the membrane is in contact with the pressurized feed, while the other side is kept at atmospheric pressure. The operating pressure depends on the membrane properties and increases as the membrane pore size decreases. Based on the pore size, different processes can be carried out, like microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, and all find relevant applications in water treatment. These membrane processes will, in fact, reject all species contained in water which are bigger than their pore size. Nanofiltration membranes can be charged and the separation occurs also in terms of Donnan exclusion. By MF it is possible to remove particles, colloids, and bacteria from water, by UF also viruses and macromolecules (like proteins), by NF also divalent ions and, finally, by RO also monovalent ions. This means that a large spectrum of water treatment can be covered, like the clarification of beer and wine or stream sterilization (MF), macromolecules recovery and fractionation (UF), water softening (NF), and desalination (RO). Table 1.2 summarizes the main characteristics of the membrane operations described.

At the exit of the membrane units, a permeate stream rich in water and a retentate stream rich in the rejected species are collected. Typical water recovery factors of MF and UF are 90%, whereas around 70 and 45% are those of NF and RO, respectively. As the membrane structure becomes denser, the rejection of species is enhanced and the retentate side becomes more concentrated, with a consequent increase of the osmotic pressure. This implies that higher operating pressures must be applied to ensure the water permeation through the membrane and, then, there is

Table 1.2 Main characteristics of pressure-driven membrane operations

Membrane operation	Pore size (μm)	Pressure (bar)	Rejected species	Main applications
Microfiltration	1.0–0.1	0.5–2	Particles, colloids, bacteria	Clarification and sterilization
Ultrafiltration	0.1–0.01	1–5	All the above plus viruses and macromolecules	Macromolecular recovery and fractionation
Nanofiltration	0.01–0.001	3–30	All the above plus divalent ions	Water softening
Reverse Osmosis	<0.001	10–100	All the above plus monovalent ions	Desalination

an increase of the energy consumption. The water recovery factors identified for the single unit are, therefore, the result of a trade-off between the productivity and the energetic demand of the membrane system.

Among the different types of water treatment in which pressure-driven membrane operations find application, desalination of sea and brackish water by RO is today one of the examples of successful implementation. The number of desalination plants based on the use of RO membranes is, in fact, quickly growing worldwide, replacing the thermal plants that are characterized by high values of energy consumptions and costs [17]. For an efficient process, it is important to ensure a constant performance of the RO units, and this can be obtained by controlling during their operation issues like scaling, biological, and particulate fouling. Besides the adoption of periodical backflushing and cleaning procedures, the identification of appropriate pretreatments is crucial to guarantee an adequate performance. In the recent past, it has been demonstrated that membrane operations can also well compete with conventional pretreatments: by using MF/UF units before RO. In such instances, the use of chemicals is reduced as well as the pretreatment footprint [18–21]. Furthermore, the RO feed is now the MF/UF permeate and, therefore, has a good quality. This means that the RO unit can work at lower operating pressures with higher flux and for longer time (reduction of costs). More recently, Membrane Bioreactors (MBRs) have been also under investigation for a possible use in the RO pretreatment line to improve the organic removal efficiency and, then, to reduce the biofouling issues during the process [22]. MBRs combine MF/UF units, and sometimes also NF, with the action of microorganisms able to decompose the organic matter. Often MBRs work in the submerged configuration with the membranes immersed into the liquid feed and the permeate recovered by a suction pump at low trans-membrane pressure (0.05–0.5 bar) [23, 24]. MBRs have been recognized as Best Available Technology (BAT) in some countries for municipal water treatment [25, 26], being more compact, showing shorter start-up time, providing a better effluent water quality and efficiently working in a wider range of operating conditions (like sludge concentration, volumetric load, etc.) than conventional activated sludge. Due to the increased awareness of health risks associated with the long-term exposure to arsenic-contaminated drinking waters, the application of membrane technology for the treatment of waters contaminated by arsenic has been also investigated, as alternative to conventional methods mainly based on adsorption and coagulation/precipitation [27]. By choosing the appropriate membrane material and the operating conditions, good rejection values for As(V) were obtained by NF and RO [28, 29] with a reduction of the chemical consumption and no need of disposing the sludge nor the adsorbent after its denaturation.

The agrofood and beverage industry successfully employs pressure-driven membrane operations for aqueous streams purification and fractionation and concentration of components. By using gentle technologies, like membranes, it has been possible, in fact, to recover products of interest, preserving their quality. For example, by integrating UF and two-step NF, it has been possible to obtain from artichoke aqueous extracts to concentrate streams, one rich in phenolic compounds the other in sugar, and a permeate consisting of purified water, able to be recycled. Moreover, the total antioxidant activity of the phenolic concentrate was significantly higher than that of the extract (47.75 mM trolox vs. 5.28 mM trolox) [30].

Similarly, it has been demonstrated that the proper combination of different membrane operations can be an effective solution to the management of Olive Mill Wastewaters (OMWs). These streams have, in fact, negative impacts on the environment, due to their high COD and phytotoxic properties, and, therefore, must be treated before their discharge. Nevertheless, polyphenols contained in these waters, if recovered, can be of interest for food, pharmaceutical and cosmetic industry. In this respect, Russo et al. [31] applied first a microfiltration of the OMW, then sent the MF permeate to two UF steps and, finally sent the UF permeate to a RO unit. The following streams were obtained: the MF and UF retentates to be used as fertilizers, the RO retentate, rich in purified low molecular weight polyphenols, to be used in the processing industry and the RO permeate, to be reused.

1.6.2 Membrane Contactors

Membrane contactors generally use microporous (0.1–0.5 µm) membranes to promote the separation. However, with respect to microfiltration where the membrane “establishes” species that can or cannot pass through based on their size, in membrane contactors the membrane is used only as inert barrier between two phases, providing their contact at the micropores mouth. Hydrophobic membranes are often employed to exploit this idea, although hydrophilic ones can also be applied, depending on the involved phases [32]. In these systems, there is no need to apply external pressure, because the mass transfer occurs simply by diffusion from one phase to the other and the driving force is given by a difference in concentration or partial pressure between phases. Therefore, with membrane contactors it is possible to carry out gas–liquid operations and liquid–liquid extractions (Fig. 1.4a), as well as distillation (Fig. 1.4b), that traditionally are conducted in packed towers, bubble and distillation columns. In particular, distillation can occur by creating a difference of temperature between the aqueous feed and the strip stream (Direct Contact Membrane Distillation-DCMD) or by sending a more concentrated strip stream at the same feed temperature (Osmotic Distillation-OD). Moreover, the distillation can also be promoted by applying vacuum (Vacuum Membrane Distillation-VMD) or sending a sweep gas (Sweep Gas Membrane Distillation-SGMD) at the permeate side.

With respect to conventional units, membrane contactors show different advantages, like the higher interfacial area per unit volume (high compactness), the uniform and constant interfacial area, the possibility of varying independently the stream flow rates without problems of flooding or foaming inside the device, and elimination of phase separation downstream, thanks to the presence of the membrane that avoids their mixing during the process. The membrane lifetime, the need of pretreatment to reduce fouling issues, and the higher mass transfer resistance offered by the membrane are some of the drawbacks. Nevertheless, the huge amount of benefits that can be obtained by using membrane contactors boosted their development in the recent past through the design of new materials, membranes and modules, and the identification of specific pretreatment protocols. Table 1.3 shows the main applications of membrane contactors for water and wastewater treatment.

One of the first successful applications of membrane contactors was the production of ultrapure water for the semiconductor industry. By using hydrophobic membranes, the aqueous stream was blocked at one side of the membrane, while the

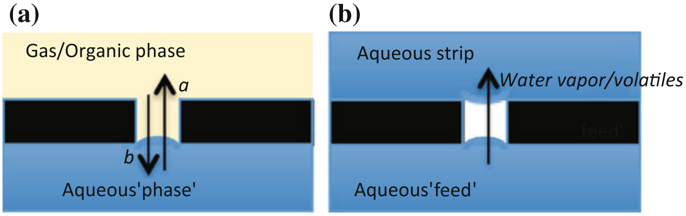

Fig. 1.4 Transfer of species between gas/organic and aqueous phases through a hydrophobic microporous membrane (**a**). Transport of water vapor and volatile species through the dry micropores of a hydrophobic membrane (**b**)

Table 1.3 Main applications of membrane contactors in water and wastewater treatment

Operation	Main applications
Gas–liquid transfer	Deoxygenation for boiler feedwater; ultrapure water production for semiconductor industry; water ozonation; sparkling water production
Liquid–liquid extractions	Extraction of aromas and of species like Cu, As, Cr(VI), etc.
Membrane/osmotic distillation	Purification and concentration of contaminated waters and wastewaters; sea and brackish water desalination

other side was subjected to stripping gas (nitrogen) and/or to applied vacuum, in order to remove dissolved oxygen from water down to the ppb range. No chemicals were needed and the system was much more compact than the conventional vacuum towers [33]. The possibility to significantly reduce the chemical consumption for the oxygen and pH control in desalination was also proven [34]. In this work, seawater was processed in a membrane contactor where a gaseous stream was sent for the combined removal of dissolved oxygen (that was stripped from the seawater toward the gas phase) and pH control of seawater. The pH reduction was made by sending gaseous CO_2, which was solubilized into the liquid stream, whereas the pH increase was reached by sending N_2 that stripped both dissolved O_2 and CO_2 from the liquid stream. In this way, a significant saving of chemicals, like sodium sulfite for oxygen removal and caustic soda and sulfuric acid for pH adjustment, was achieved. Hydrophobic membranes have also been employed for the removal of ammonia from wastewaters, by sending as extractant sulfuric acid. With respect to conventional methods that usually produce a secondary waste stream, membrane contactors allow to efficiently strip the ammonia (removals up to 95%) and convert it into ammonium sulfate (that can be sold as fertilizer) in the same unit [33].

The efficiency of membrane distillation for the treatment of a large variety of liquid streams has been also demonstrated in the past years [35, 36]. In membrane distillation the feed to be treated is often warmed up to increase the driving force across the membrane (higher water vapor pressure at the feed side). Nevertheless, typical operating temperatures fall within the range of 50–70 °C, which can be conveniently achieved by renewable energies, like the solar energy. Moreover, the process is not affected by osmotic limitations, as for RO, and high recovery factors can be obtained. With respect to conventional distillation column, membrane distillation units allow a significant space saving. Since only volatile species are transported through the membrane pores, high-purity water can be collected as permeate. For example, both pentavalent and trivalent forms of arsenic are kept at the concentrated side, avoiding the need of a pre-oxidation step for converting As(III) into As(V), which is usually better rejected by other treatment methods (NF and RO included). Membrane distillation thus reduces the use of chemicals (ozone, hydrogen peroxide or chlorine are often employed) and the complexity of the plant [37–40].

1.6.3 Coupling Pressure-Driven Membrane Operations with Membrane Contactors

To date, membrane processes show high potential for efficiently carrying out water and wastewater treatments. Their performance can be further improved by the integration of different membrane units. It has already been described about the reduced fouling and increased water recovery factor that can be achieved by using MF/UF as pretreatment stage of RO. Further benefits can be gained by also integrating membrane contactors.

For example, in desalination there is the need to increase the freshwater production, to produce desalted water that complies with the current legislative requirements, to find solutions for the management and disposal of the produced brine. In desalination plants, the MD unit can operate on the RO brine: more freshwater is produced (water recovery factors up to 90%) and the volume of brine to be disposed is highly reduced [41]. Moreover, by pushing the distillation up to crystallization, valuable salts can be recovered and the Zero Liquid Discharge (ZLD) approached [42]. Reverse osmosis membranes, although efficient in rejecting the major part of the species present in the stream, do not show high rejection values toward Boron (at the seawater pH, it is present as undissociated boric acid) for which the World Heath Organization (WHO) has imposed the concentration limit of 0.3 ppm. Actual RO plants work with more stages operating at different pHs: after the first stage at neutral pH, the second stage operating at high pH (at which boric acid dissociates) and boron-selective resins are used to meet the desired boron concentration [43]. The potential of a liquid–liquid membrane contactor for the control of the boron content of the final water was confirmed by Criscuoli et al. [44]. The membrane contactor used a hydrophilic membrane to remove, by diffusion, the boric acid from the feed (the RO permeate) to a distilled water stream (distilled water was selected as the extractant, to avoid the use of solvents inside the plant) that was continuously purified and recycled back to the membrane contactor. In this way the high pH RO stage and the resin were avoided, with a consequent reduction of the plant complexity and chemical consumption.

The valorization of wastewater streams by the collection of both purified water and products of interest can also be improved by introducing membrane contactors in the plant. For example, flavonoids were recovered from orange press liquors, while purifying water, by integrating UF, NF, and OD. The OD was able to produce a stream concentrated in flavonoids, of interest for nutraceutical and pharmaceutical applications [45].

By treating the wastewater coming from textile industry in an integrated membrane system based on MF, NF, and MD, it was possible to obtain freshwater to recycle, an organic fraction to energetically valorize and salts to use in finishing baths [46].

Figure 1.5 summarizes the major benefits that can be obtained by integrating pressure-driven membrane operations and membrane contactors.

1.6.4 New Metrics

Water indicators were previously described as means to assess the sustainability of water treatment systems. Recently other parameters, which can be considered as further granularity of the indicators suggested earlier, have been included in the analysis of the plant performance. They are the size and the weight of the plant together with its flexibility and modularity. These can be considered components of investment costs. In particular, specific metrics were defined and applied to a case

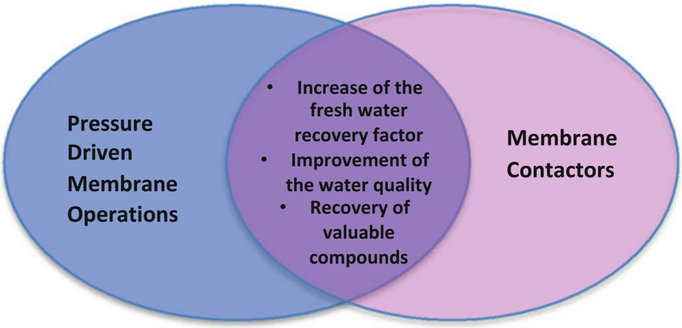

Fig. 1.5 The integration of different membrane operations as a means to improve the performance of the process

Table 1.4 Link between new metrics and sustainability domains

New metric	Sustainability domain	Remarks
Productivity/size ratio	Economic-environmental	Smaller sizes are beneficial for land saving
Productivity/weight ratio	Economic	Lower weights reduce transport and installation costs
Flexibility	Economic	High flexibility allows to handle variations in the operating conditions as well as different processes in the same plant
Modularity	Economic	High modularity helps in plant scale-up and scale-down

study, to take into account these parameters when comparing the performance of membrane operations with that of conventional units [47]. Due to the decreased availability of land its use has to be carefully managed and, therefore, smaller plants must be preferred, at parity of productivity. Similarly, lighter plants are better because of lower costs for transport and installation. A reduction of costs is also obtained if the plant is versatile and able to handle variations that can occur during the life of the plant (high flexibility) and easy in its scale-up or scale-down (high modularity). In this respect, two flexibility metrics were defined. The first one compares the membrane and conventional operations in terms of their capability to be applied in different types of production: the higher the number of operations that can be carried out in the same unit, the higher the economic benefit when a redesign of the production line is needed. The second one makes the comparison in terms of the ability to cover changes in the operating conditions (e.g., changes in the feed stream composition). Finally, the modularity metric compares the variation in size of the plants needed to handle a variation in the productivity. Table 1.4 summarizes the new metrics evidencing how they can be linked to sustainability.

Table 1.5 Sustainability of membrane operations

Membrane property/performance	Sustainability domain	Remarks
Low operating temperature	Economic-environmental	Low-energy consumptions. Renewable energies are sufficient for the typical temperatures used in MD
No use of chemicals/reduced chemicals use by membrane integration	Sustainable	Low costs, environmental and human health impact. High work safety
High quality of the produced water	Economic-societal	Meeting the legislative requirements. Preservation of human health
Recovery of valuable products in mild operating conditions	Sustainable	Conversion of waste streams into a resource. Preservation of product properties
Low sludge/brine production	Economic-environmental	Low costs. Low environmental impact
High separation efficiency for a large number of species in the same unit (e.g., MD able to reject all nonvolatile compounds)	Sustainable	Reduced number of units needed to carry out the separation. Meeting the legislative requirements. Preservation of human health
No moving parts	Societal	High work safety
Low size	Economic-environmental	Low footprints lead to a reduction of land use
High flexibility	Economic	High flexibility allows to use the same plant in different conditions/needs
High modularity	Economic	High modularity helps in plant design

1.7 Concluding Remarks

Membrane operations have been demonstrated to be efficient systems for the treatment of both water and wastewater. Membrane systems do not present moving parts, do not need the use of chemicals, work at ambient temperature (except membrane distillation), and have high separation efficiency together with high surface/volume ratios (small size). Therefore, they contribute to sustainable development, as reported in Table 1.5.

In other industry sectors that handle materials, such as oil and gas, chemicals, fertilizers, cement, mining and metal processing, etc., harmful compounds that can pollute the environment largely appear as inputs. Part of the offending chemicals and materials is emitted to the environment because of the inability of present-day technologies to achieve zero discharge at a cost that either the investors can justify in a globally competitive market or the consumers can find them affordable.

These industries also use water as an input and the process waters carry many of the pollutants that need to be treated by appropriate processes. Wherever they are applicable, membranes can have a sustainability advantage over other processes. For potable water, the treatment challenges are much diminished as the input water is relatively cleaner to begin with. In this chapter water disinfection was not discussed, though it is of paramount importance. Membrane processes that treat drinking water or wastewater are not exempt from the responsibility to disinfect for pathogens. Before a membrane process is put in operation, however, this issue needs to be addressed, except where for intra-plant recycle it may not be a great issue in all situations. In the case of any other technology this is always the last step before the water is either used for drinking or for recreation, or for discharge to a river. The situation with membrane technology therefore is no different. Thus, a comparison for sustainability is fair with other water treatment technologies, as all these technologies need a disinfection validation.

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Chapter 2
LCA for Membrane Processes

António A. Martins, Nídia S. Caetano and Teresa M. Mata

Abstract This chapter presents an overview of the current state of the art concerning the application of life cycle assessment (LCA) to assess and improve the environmental performance and sustainability of processes that use or are based on membrane technologies. A presentation of the LCA methodology is made, based on the current framework defined by the ISO Standard, focusing on the main aspects and how LCA can be applied to a given product or process system. A review of the available studies was done for membrane based or systems in which membranes have an important role, focusing in water treatment process, either for human and industrial application or wastewater treatment. The analysis shows that the application of LCA is still limited in membrane process, and more work still needs to be done, for example, taking into account the manufacture and final disposal/recycling of the membranes and their corresponding process modules, and to properly asses how membranes may increase the sustainability of existing processes by replacing existing technologies with larger environmental impact. As the need to evaluate the environmental impact and sustainability of new processes increases, the application of the LCA methodology will become more common both in process design and/or process operation.

Keywords Membrane technologies · Life cycle assessment · Sustainability evaluation · Environmental impact · Water and wastewater treatment

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2.1 Introduction

It is increasingly consensual that human development, coupled with the current patterns of production and human consumption, has resulted in significant environmental impacts. They can be of a local nature, for example, water and air pollution, or global, for example, global warming mainly due to burning of fossil fuels for energy generation. Recognizing that a course of change is needed at all levels, national, regional and city level, international organizations and governments have proposed and are implementing strategies to tackle the challenges of a more sustainable development [1–3].

Although the problems are global, the answer strongly depends on the context, in particular, on the local conditions and the stakeholders involved. For instance, industry tries to be increasingly more environmentally friendly and to fulfil its regulatory and legislative obligations without reducing its market competitiveness. On the other hand, citizens in general are better informed about the environmental issues, and demand an improvement of the environmental quality without compromising significantly their quality of life. Therefore, new or improved production processes are needed to supply the products and services needed for a progressively more globalized and developed world.

While the questions of production and consumption must be considered simultaneously, in this chapter the focus is on production systems. Currently, this is a key research area in the sustainability area that combines the expertise of many scientific disciplines, including engineering, economy and the social sciences.

More sustainable production systems, or at least with lower environmental impacts, require the retrofitting of existing processes or the development of new ones. Possibilities involve the utilization of renewable raw materials and/or energy instead of non-renewable, or the utilization of new technologies. Among them, membrane technologies are one of the best possibilities, currently seen as having great potential for improving the sustainability of current production systems. In some industrial activities membranes are already extensively used, as for example in water purification. Their utilization is increasing and new applications are being considered and developed for a wide variety of applications [4].

Membrane processes are a class of separation processes used to remove selectively components from a solution or suspension. The separation involves the permeation of a fluid through the membrane, in which certain components, either chemical compounds and/or solid materials, are retained. The product stream enriched with the components that cross the membrane is called permeate. The other stream is called retentate. Key factors influencing the separation are the components size (even for chemical compounds), the membrane characteristics (for example its porosity, pore size distribution, electrical charge, among others) and the magnitude of the driving force. A more detailed description about applications, operational and physico-chemical characteristics of membrane systems is beyond the scope of this work that focuses on their environmental performance, but it can be found in the literature [5–8].

When compared with other separation processes that fulfil the same tasks, membranes have some advantages, being some of the most relevant listed below [9].

- They normally operate at low temperatures and/or pressures, thus reducing the energy consumption. This is a relevant issue in process dealing with temperature sensitive raw materials and/or products, for example, food processing.
- Membrane characteristics can be fine-tuned to address specific separation requirements.
- Membrane can be made from a wide variety of materials, allowing the development of robust processes adapted to the process conditions and/or components involved [10].
- Membrane processes do not require the use of solvents.
- Membrane units can be made in a compact form, reducing the space needed to their installation and operation.
- Replacement of membrane units and/or parts can be done easily and fast, as they are built in a modular fashion.
- Simpler scale-up, by just adding or removing membrane modules/units, according to the processing needs.
- Although currently in most of the membrane processes the separation is purely physical, it is possible to functionalize the membrane, allowing, for example, the coupling of chemical reaction with separation. This is a form of process intensification, resulting in more efficient and compact processes. Currently this is a very active area of research, in which significant progress is expected in the near future [11–13].

Notwithstanding the advantages, the application of membranes in practice poses some challenges, and may have some environmental impacts that must be accounted for. Some of the most relevant include:

- Fouling that reduces the membrane capacity to perform the desired separation. Possible reasons include the accumulation of the contaminant in the interface between the fluid and the membrane, increasing the resistance to mass transfer. Other possibility is membrane degradation that may lead to membrane replacement.
- Membrane cleaning may be difficult or even impossible.
- Retentate or permeate disposal, depending if it is intended to remove or concentrate a certain component.

Thus, membrane processes and/or membrane unit operations are currently seen as more environmentally friendly options to perform a wide range of tasks, for instance, water processing, for either human/industrial consumption or wastewater

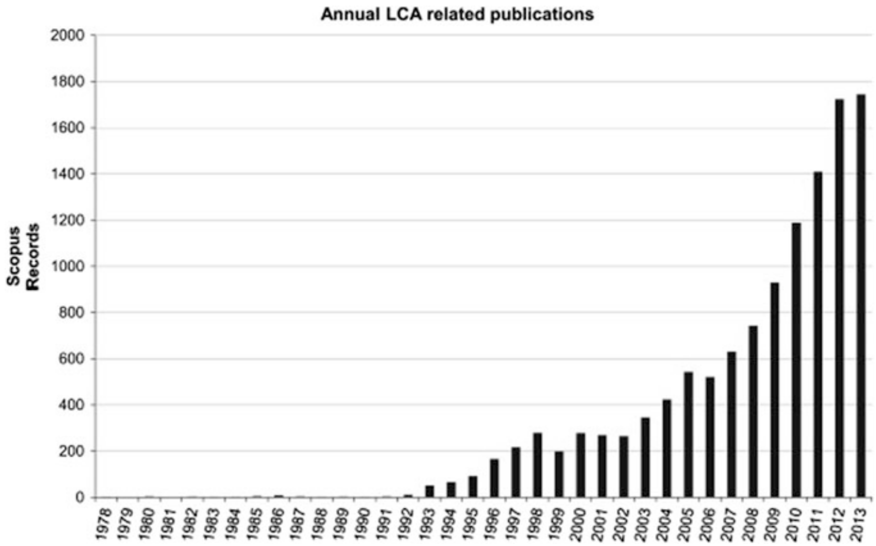

Fig. 2.1 Number of LCA related publications per area. Reprinted with the permission from Ref. [22]. Copyright 2015 Elsevier

treatment (WWT), food processing, fuel cell operation, among many others. They are even considered in some processes as the best available technology (BAT), for example, in the production of chlorine using electrochemical processes [14]. Many examples of studies and/or applications of membranes that claim to be more sustainable or contribute to sustainable development can be found in the literature [9, 15–20]. However, when designing and/or retrofitting a process in which membranes are a key part of the system, one needs to have objective environmental evaluation tools, for example, to identify which are the best options to use membranes and how they can improve existing processes. Of the various possibilities, life cycle assessment (LCA) has emerged in the last decades as the one of the relevant framework to assess the environmental impact of a product/service or a process [21, 22]. Figure 2.1 presents the evolution of the total number of LCA-related publications from 1978 to 2013 [22]. The figure shows an increase, in particular in the last decade, demonstrating that LCA is becoming a very relevant tool to evaluate the environmental impact of products and processes, with applications in a wide range of areas, even including legislation and/or regulations [22, 23].

In the next session, a brief description of the LCA methodology is given, highlighting the key aspects of the methodology, how it can be applied in practice, and extensions of the standard methodology.

2.2 Life Cycle Assessment (LCA)

LCA is a systemic methodology with the main goal of quantifying the potential environmental impacts of a product/service or process through its life cycle stages [24, 25]. LCA allows a complete analysis of a given product or process system taking into account all the life cycles associated with it, from extraction of raw materials to final disposal, making it possible to identify the steps with larger environmental impact in which improvements are needed. Although variations are possible, usually a LCA study includes the following steps: extraction and preparation of raw materials, manufacture, distribution, use, repair/upgrade/maintenance, and final disposal or recycling. This corresponds to the most general case, a cradle-to-grave analysis. Depending on the goals of the study and availability of data and/or impact assessment methodologies, it is possible to define other system boundaries for the LCA studies, for example, cradle-to-gate studies that do not consider distribution and consumption of products.

Accounts of the evolution of LCA in the last four decades can be found in the literature [22, 23], showing that the interest and application of LCA is growing, as shown in Fig. 2.1. Historically, LCA started between late 1960s and beginning 1970s to address the environmental impact of packaging systems, in particular for beverages [22]. Starting in the 1990s, there was an effort from some governmental and international organizations to define guidelines or even standardize how the LCA studies are done, allowing, for example, an objective and unbiased comparison of studies made by different organizations. These efforts resulted in a set of ISO standards, part of the ISO 14000 environmental management standards: ISO 14040:2006 [26] and ISO 14044:2006 [27].

2.2.1 Methodology Description

In this section, the key aspects of the LCA methodology will be briefly described. A full and in-depth description of the LCA methodology and its foundations is outside the scope of this chapter. Detailed descriptions of the LCA methodology and how it is applied in practice can be found in the literature [28–30].

The fundamental goals of an LCA study are as follows:

- Make a compilation of all relevant material and energy inputs and environmental emissions;
- Quantify the potential environmental impacts resulting from the system inputs and outputs;
- To interpret the results and to identify hotspots in the process, support decision-making, among others possibilities.

To fulfil these goals, the LCA standard ISO 14040:2006 defined four steps (Fig. 2.2): (1) Goal and scope definition, (2) Inventory analysis, (3) Impact

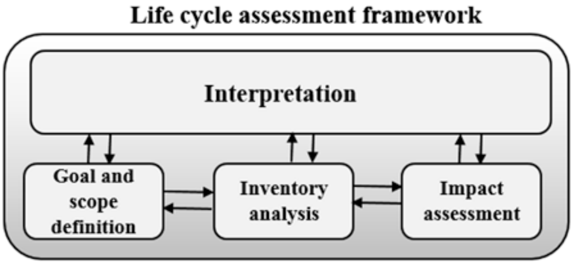

Fig. 2.2 LCA main steps, according to ISO 14040:2006

assessment and (4) Interpretation. The three steps in bottom line of Fig. 2.2 are normally performed sequentially, from left to right, as they depend on each other. Although the interpretation step deals mainly with the analysis of the impact assessment results, during a LCA study it is normal to critically assess the assumptions made in each step, the data quality and other relevant issues throughout the study.

2.2.1.1 Goal and Scope Definition

In the goal and scope definition step, the study purpose is described and its main goals are defined [31]. Depending on the context and specific circumstances in which the study is made, different types of studies are possible depending on what are its main aims, such as:

- Determine which life cycle stages contribute the most to a product/service or product whole life cycle impact, for which a complete life cycle is required.
- Compare different products/services or processes but with similar purposes.
- Determine the environmental consequences of changes in the process, for example, changes in the raw materials used or by using other process units.
- Obtaining the Environmental Product Declaration (EPD) of a product, for which specific regulations may apply.

In order to be able to compare different products or production systems, a common form of comparison is needed. This is done by defining a functional unit (FU), defined as a measure of the system main function or performance [32]. The study results are expressed in terms of the FU, ensuring that objective comparisons can be made between different product/service or processes systems. The definition of a FU also reduces any potential dimension effects, for example, when a product can be produced using processes with significant capacity variations. When performing a comparative LCA study, it is often necessary to define a reference flow that corresponds to a quantification of the product flows, including parts, necessary for a given product/service or process system to have the same performance defined by the UF [33].

Other key issues considered in the first step include:

- Definition of which relevant environmental impacts will be evaluated in the study and which methodologies will be used for it. This ultimately depends on the study objectives and the nature of the process. Guidelines for the definition of the adequate impact categories for a given study are available [33–35].
- Definition of the system boundary. As many products/services or processes involve many parts usually strongly interconnected, a selection of the most relevant must be done. This procedure ultimately depends on the assessment goals and the criteria defined.
- Assumptions concerning the study timeframe, types of process units, geographical settings, data sources, among others, strongly depend on the nature of the product/service or process considered.

The system definition and study timeframe must take into account if the study is dealing with a product/service or with a process. In the first case, that corresponds to most LCA studies performed and available in the literature, the various life cycle stages maybe be classified according to their position in the supply/production chain: extraction of raw materials, processing, distribution, consumption/usage and final disposal/recycling. An LCA study may be classified according to the life cycle stages considered, cradle to grave (full LCA) if all the previous steps are considered, cradle to gate (e.g. when the use and disposal steps are not considered) and others. Between the various life cycle stages transportation of raw/processed materials or products parts may take place. The distance travelled and mode of transportation depends on nature of the materials involved, local resources availability, among other issues.

In the case of processes, the system parts can be classified as follows: design and development, process construction and implementation, process operation and final dismantling. The timeframe is also dependent on the nature and type of the process, but it is usually much larger when compared to product/service systems, normally more than 10 years.

2.2.1.2 Inventory Analysis

In the inventory analysis phase, an input–output accounting is done, as complete as possible, of the materials and energy consumption, corresponding to the inputs, and to the emissions and waste generated during the life cycle, corresponding to the outputs. It involves three sub-steps done sequentially, as shown in Fig. 2.3:

In the first sub–step, a process flowchart is built that includes all relevant system subparts, such as transportation steps, raw materials processing, among others. Then, the inputs and outputs are identified, corresponding them to the fluxes of materials, waste and energy through the system boundary. The interrelations between the various system parts, in particular fluxes of energy and materials, should be clearly defined. Although not required, a visual diagram should be drawn, as it helps in better identifying and highlighting the relevant aspects of a given system.

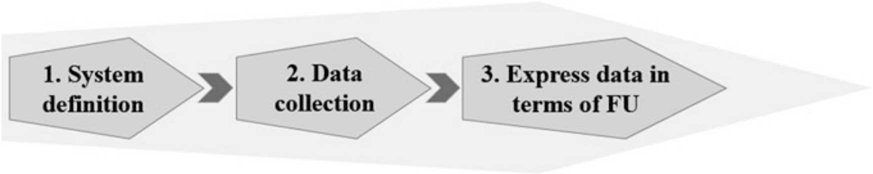

Fig. 2.3 Substeps of the inventory analysis

The next sub-step corresponds to data collection, essential to be able to evaluate the potential environmental impacts in an objective way. In this process, raw materials and energy consumptions, and emissions resulting from the system activities are accounted for. Primary data, obtained, for example, from the real process units or product utilization is preferred. When it is not available, secondary data from the literature and/or databases or even the results of process simulation may be used whenever necessary. Energy usage impacts should take into account the local/regional conditions through the utilization of an adequate energy mix. In the last sub–step, each input and output, either of materials or energy, is expressed as a function of FU. The calculations may involve conversion of units and even solving material and/or energy balances whenever necessary.

The previous sequence is general but in practice it must be applied with caution. Problems in the inventory may arise when a company or production system produces a wide variety of products, or when process units are used and/or shared by different production systems and only the overall values of energy and materials are available. In these situations, it is necessary to perform an allocation procedure that consists in accounting only the inputs and outputs that correspond to a given product or service. Depending on the system and production process, several possibilities are possible, for example, allocation by mass, by value or by system expansion as recommended by the ISO LCA standard [28, 30, 36]. In some cases it may not be easy to define objectives and consensual allocation procedures are adequate for a given product/service or processes.

Other potential problem concerns data adequacy and quality, in particular, when secondary data from life cycle databases or the literature is used. Although in many cases, they are representative of real processes, when the technologies used and/or the local conditions are significantly different, the data may not be representative of the product/service or process system under study. In this situation, an effort to obtain primary data should be done, or a complete sensitivity analysis should be done, valuable to identify which aspects and/or emissions are more to the overall environmental impact. Also relevant, especially in systems with many input and output streams, is which consumptions and emissions should be considered. In practice, it is usual to define a cut-off value or percentage, bellow which the consumptions or emissions are not accounted. However, this procedure should be done with care, as the environmental impacts of different compounds are different and some significant consumptions and/or emissions may be not considered at all.

The organized input–output data is called the life cycle inventory (LCI), and includes a detailed description of all the materials and energy consumptions (corresponding to the system inputs) and emissions and waste streams generated (corresponding to the outputs) connected with a product/service or process life cycle. The data can be used to compare different processes or products/services directly, for example, energy consumption or emission of specific pollutants, a procedure in which expressing the inputs and outputs as a function of FU ensures an objective comparison. In this case, the study is called a life cycle inventory analysis (LCIA). However, usually the data and information gathered is used as a basis to evaluate the potential environmental impacts.

2.2.1.3 Impact Assessment

After creating the LCI, the potential environmental impacts can be determined, either for the overall life cycle or for the individual subparts of a system, depending on the specific goals of the study. According to current practice and the ISO Standard, four sub-steps can be defined, the first two are mandatory and the remaining two are optional, as shown in Fig. 2.4.

In the first sub-step, called classification, the various material and energy inputs and outputs are assigned to environmental impact categories previously defined in the goal and scope definition. Although there is some flexibility in the definition of impact categories, depending on the main environmental impacts associated to each product or process system [33, 34], the following set is commonly encountered: Global Warming Potential/Carbon Footprint, Ozone Depletion Potential, Eutrophication Potential, Photochemical Potential, and Acidification Potential. To each impact category corresponds an environmental indicator.

In the second sub-step, called characterization, each impact category is evaluated. The value of the corresponding environmental indicator is calculated using an impact assessment methodology, defined in the first step of the LCA methodology. One common approach involves the use of conversion factors, also known as characterization or equivalency factors, to convert the LCI results in values that can be compared between system parts or even other studies. Extensive lists of characterization factors can be found in the literature [37]. An example is the indicator Global Warming Potential/Carbon Footprint, which is calculated and expressed in

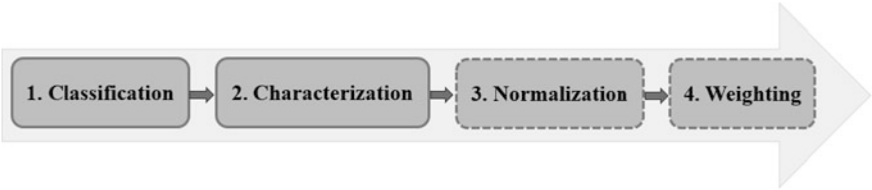

Fig. 2.4 Substeps of the impact assessment step

terms of mass of CO_2 eq. emitted to account for the different contributions to the greenhouse effect of different gases, for which emission factors were proposed by the IPCC [38].

When performing a LCA study or a process an interesting arises on how are the environmental impacts of the construction and/or dismantling phase evaluated and allocated to the functional unit. Those life cycle steps have a small duration when compared to the overall study timeframe, usually the process lifetime. If the UF is defined as a unit product, most of the times an objective measure of the system duration, it is normal to allocate the impact of the construction and dismantling to the total quantity of product produced, thus diluting in time the environmental impacts of those two life cycle steps.

The other two sub-steps are optional and can be done independently of each other. In the normalization sub-step, the impact assessment results are normalized using a reference factor. For example, they can be related to the environmental impacts of one product or specific life cycle stage. This procedure may clarify and simplify the interpretation of the results, highlighting, for example, differences not easily seen in non-normalized data.

The weighting sub-step is performed in some studies, especially when products or processes are compared with each other. It may not be easy to determine which product/service or process is better as no clear pattern can be extracted from the indicators values. Also, when presenting the LCA study results, in particular to non-specialists, the utilization of many indicators can be confusing and mislead the audience, a situation that may occur in decision-making processes based on LCA results.

Weighting tries to avoid these problems by combining all indicators in a single score/index. This process uses factors that reflect the relative importance of each environmental impact. Their definition is both a political and a scientific process, in which all relevant stakeholders play a part. Thus, no consensual weighting scheme exists. Hence, many practitioners do not apply weighting to the indicators. Although the report is more complex and may be ambiguous in some cases, there is no loss of information due to the weighting process.

2.2.1.4 Interpretation

The previous three steps follow a logical sequence. Albeit the interpretation step is the last one, from a practical point of view it occurs throughout the entire study, dealing with the questions of assumption assessment, clarification and adjustment, sensitivity analysis, and data and results checking. As the fourth and last step, current practice and the ISO standard consider two main goals:

- Analyse the results of the impact assessment in order to: reach conclusions, identify life cycle hotspots and/or which life cycle stages have the most significant environmental impacts, identify weakness/limitations, propose recommendations and/or improvements, find what are the main study conclusions, among others.

- Deliver a transparent and objective presentation of the LCA study, taking into account the goal and scope of the study.

A fundamental part of the interpretation phase is the analysis of the data used and how the calculations were performed, in particular, its completeness, reliability, sensitivity and consistency. In many LCA studies, a sensitivity analysis is performed in which various aspects are varied, such as assumptions, data sources, characterizations factors and data ranges. While this process makes a LCA study more complex, it provides extra insight on the results and supports the recommendations and decision-making process.

A critical review is also performed in many cases, for example, to fulfil regulation obligations in the issuance of environmental product declarations. It consists in the critical scrutiny by a third party, either a specialist or an independent organization of the LCA study. The main goals are to identify possible aspects that need to be improved, lend credibility to the LCA study, and avoiding potential bias resulting from the specific interests and background of practitioners and/or organization that commissioned the study.

2.2.2 Extensions

LCA, as defined in the ISO standards, only considers the potential environmental impacts of a product/service or process system to support, for example, decision-making and/or the implementation of measures to improve their environmental performance. While relevant, from a sustainability and even practical point or view, the results of an LCA study have a limited scope and potential, as the other key dimensions of sustainability are not taken into account, in particular, the societal and economic dimensions. Moreover, in practice LCA is used more often to assess products than process, as their life cycles are easier to define and it is easier to improve the overall system based on the study results.

2.2.2.1 Extended Methodologies/Frameworks

To allow the incorporation of other non-environmental related issues, some extensions of the LCA ISO Standard were proposed and are used, in practice, to complement the basic LCA framework. A comparison between the proposed extensions of the standard methodology is presented in Table 2.1, summarizing their aims/goals, main advantages and drawbacks.

The LCA methodology as defined in the ISO standards does not consider the time dimension, as life cycle stages and process system are fixed in time. This corresponds to an attributional LCA approach, as the environmental impacts are determined and attributed to each life cycle stage. It allows practitioners and decision-makers to identify environmental hotspots that should be considered for

Table 2.1 Extensions of the ISO LCA standard

Extension	Goals	Methodology characteristics	Particular issues
Social LCA, S-LCA, guidelines from UNEP are available [41].	Assess potential social and sociological impacts of product/service or process life cycle	Data sources: statistical census and/or economic data: jobs creation, workers income, etc. Possible indicators: local jobs created, labour practices, percentage or local jobs	Methodology follows the standard LCA methodology. The impact categories should be related to specific stakeholder groups, such as workers, consumers, local community, society and other value chain actors. There are still significant issues that have to be dealt with before S-LCA is more used in practice. In particular, in many cases objective data is not available, and there is lack of reliable and consensual impact assessment methods [42]
Life cycle costing—LCC. A code of practice was proposed by SETAC [43]	Evaluates the economic impacts of the various life cycle stages of product/service or process	The analysis includes not just the costs of raw materials and energy, but also the environmental costs. Possible indicators: cost of emissions, cost of waste treatment, etc.	In classic economic analysis of products and/or processes environmental costs are considered as externalities and not accounted in the calculations. Although it is consensual that these externalities must be accounted for, the methods available today for their estimation are limited, lack in objectivity and are not consensual

(continued)

Table 2.1 (continued)

Extension	Goals	Methodology characteristics	Particular issues
Life cycle sustainability assessment—LSCA. Guidelines for LCSA were published by UNEP [44]	Assess the potential sustainability impacts of product/service or process life cycle	Framework combines LCA, S-LCA and LCC. All indicators and data sources relevant to the previous methodologies are valid in LSCA, but care must be taken to avoid unnecessary duplication of information and/or results	As each methodology takes into account each pillar of sustainability independently, after combining their results an overall view of the sustainability of a product/service or process is obtained revealing, for example, what are the main issues that should be considered first when making decisions about products or processes. Still not significantly used in practice, but it is consensual today that a proper sustainability assessment should be based on a life cycle perspective

improvements, but it is possible to determine what will be the future environmental impacts. Consequential LCA seeks to do that, in particular assess what are the consequences of decisions and/or changes in the system under study, for example, technology changes. Contrary to the attributional LCA, the economic consequences of the changes must be taken into account. This is an important limiting factor when performing a consequential LCA analysis, as predicting the impact of changes in future systems is always complex and requires taking many assumptions, reducing the objectivity of the calculations [39, 40].

LCA and its extensions are also a key part of frameworks based on life cycle thinking (LCT). This approach tries to reduce the environmental, social and economic impacts of current human activities taking into account all the life cycle steps associated with them. This way it is possible to avoid burden shifting, and the solutions developed are closer to the optimal and reduce the overall impacts of producing, using and disposing of a product/service or process. The methodologies described before: LCA, S-LCA, LCC and LCSA, are the tools used in the LCT approach, supplying the information required for a proper decision-making.

LCT assesses the entire supply chain of a product, either upstream or downstream, and the environmental, social and economic impacts. Both qualitative and quantitative approaches can be used although the former is preferred from a management point of view. This way, LCT can help identify opportunities for improvement and support decision-making in all dimensions of sustainability.

LCT is starting to be at the core of strategies development, as it is a good way of taking into account all relevant aspects, including resources and energy consumption, stakeholders' needs and expectations, biodiversity protection, among others. Examples of practices and/or policies in which LCT plays a decisive role include: waste management, reduction of the energy consumption during the product use phase through an adequate product design, Green Public Procurement (GPP), definition of the best available technologies (BAT) for a production processes, among others [45–47].

2.2.2.2 Process Design

Although the ISO standards are easier to apply to existing product/service or process systems, they can also be applied to process design or to retrofitting of existing process, to improve their overall environmental performance. The application of LCA should start at the design stage, to ensure that the most adequate solutions are chosen. In addition, the cost of process changes is smaller in the beginning of the process design than later, in the process implementation or testing/start of operation stages [48]. As expected, the lack of data may be a significant problem, as the uncertainty in the process conditions and behaviour is large. Data from process simulations, laboratory experiments, life cycle inventory databases, scenario analysis and industrial practice can reduce the uncertainty and facilitate decision-making [48–51].

Despite the potential difficulties, it is widely recognized that LCA is a valuable tool to process design and optimization. Good reviews can be found in literature dealing with the application of LCA to chemical processes [52–54]. Frameworks and methodologies to process design including LCT/LCA principles were proposed, in particular, to account for the environmental impacts and sustainability issues whenever possible [48, 55–58]. Examples of the application of LCA in the design of chemical processes or in design criteria can also be found in the literature [59–61].

2.3 Application of LCA to Membrane Processes

Currently, the methodology of choice to assess the environmental impact of products/services and processes, the LCA methodology has already been applied to membrane-based processes or processes in which membranes play a significant role. As membranes are used in a wide range of process in various sectors of activity, this work will focus its attention in water treatment processes, in particular, for human consumption or for wastewater processing. Membranes are extensively used in the both cases to perform key steps, for example, to remove contaminants or undesirable compounds, for example salt from sea water to obtain fresh water. Other applications, such as energy applications (fuel cells), compound extraction and/or purification, gas purification, among others are only briefly presented in this chapter, even though they are increasingly important in a variety of applications.

2.3.1 Water Treatment Systems

Water treatment systems are extremely relevant from a sustainability point of view, as they help fulfil goal 6, clean water and sanitation of the UN sustainable development goals [1]. Moreover, water is fundamental in agriculture and in industry, sectors essential to satisfy the basic needs of human societies. Membrane systems or processes are already having an important role fulfilling those goals. Their importance and range of applications are expected to increase in the future, as membranes are a good option from an economical and environmental point of view when compared to other technologies.

Different technologies and system structures are used to wastewater processing or water production for human or industrial consumption. To the authors' knowledge, most of the LCA studies available in the open literature only considered one of the two possibilities, justifying the separation of the available works in two subsections, one for water treatment for human or industrial consumption, and other for WWT either of urban or industrial origin.

2.3.1.1 Human and Industrial Consumption

When considering water production for human or industrial consumption, membranes are usually used to remove contaminants that may have significant health issues or result in important corrosion and production quality concerns. For example, water softening increases the lifetime of plumbing and other flow equipment by reducing the potential for the build up of limescale, and reverse osmosis membranes can be used in this process. For human consumption, membranes are currently the main technology used in the desalination of seawater, a process increasingly important to human development, especially in regions where water resources are scarce or fresh water too polluted to be practical and economic its purification. Even tough the environmental impact of water production ultimately depends on the process conditions, according to the LCA methodology, a detailed knowledge and description of the operational conditions is not necessary. Comprehensive reviews of the utilization of membranes in water production for human or industrial consumption, in particular for desalination, can be found in the literature [62, 63].

Figure 2.5 presents a general production system to obtain water for human consumption [64]. It incorporates all relevant processes and life cycle stages, in particular, water extraction and treatment, waste disposal, chemicals and energy

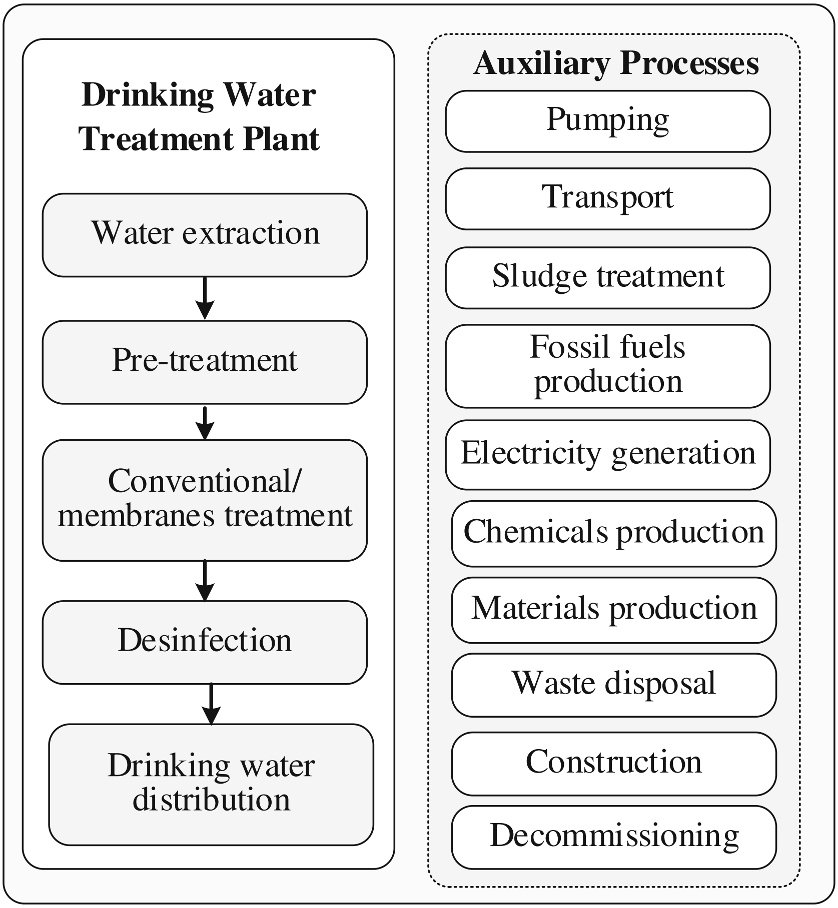

Fig. 2.5 General water production process for human or industrial consumption

production and utilization, and water distribution to the consumer. Depending on particular conditions or the final water application, some of the process units or processes presented in Fig. 2.5 may not be used. It can be seen that membranes are mainly used in the treatment stage to remove contaminants. In the case of seawater desalination that will correspond to salt removal. Membranes do not operate alone but combined with other upstream and downstream process units. Hence, when performing a LCA study of a water producing system for human consumption, membranes or membrane technologies are usually considered integrated in the process system.

Table 2.2 presents and compares the main features of some LCA studies performed for water production systems for human consumption that incorporate membrane processes and/or technologies. For each study, the following information is given: water source, FU, goal of the study, system boundaries and main life cycle

Table 2.2 Comparison of LCA studies for water production for human consumption

Source	Water Source, FU, Goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
Raluy et al. [65, 66]	Water source: sea water. FU is the daily production of 45,500 m^3/day of potable water, with 8000 h of operation per year, for 20 years operation. Goal: reverse osmosis compared with thermal evaporator technology	A cradle-to-grave analysis of the desalination process was performed. Process construction, membrane replacement and materials consumption are considered primary data from existing plants was used whenever possible. Environmental impacts were evaluated using several methodologies: CML, Eco-Points 97 and Eco-Indicator, for various environmental indicators. Calculations were performed using SimaPro software	Results show that reverse osmosis has an environmental impact an order of magnitude lower than technologies based on thermal evaporation, The influence of the energy source, in particular. electricity was analysed, showing that utilization of renewable energy can significantly reduce the environmental impact
Hancock et al. [67]	Water sources: sea water and low salinity waste water. FU: 3875 m^3/day. Goal: comparison between standard process with a new one based on forward osmosis, combining seawater desalination with water reclamation	System considers only water processing, considering also the production of membranes and materials consumption. Water preprocessing and final distribution not considered. Primary data combined with databases was used. Ten environmental impact categories were used using CML methodology and SimaPro software to perform the calculations	Results show that module design and cleaning intensity are the keys to improve the environmental impact. New process has more impact, but it is shown that with proper optimization the same environmental impact of standard process is reached
Tarnacki et al. [68]	Water source: sea water. FU: 1 m^3 of treated water. Goal: compares two desalination processes: standard based on reverse osmosis and a new proprietary process	Several scenarios for localization and energy sources were analysed. A cradle-to-grave analysis was done, including construction and decommissioning, but without membrane production. Data from inventory databases was used. Impacts were assessed using Eco-Indicator, CML and Eco-points using GABI	Energy production is the dominant source of environmental impacts. Heat recovery and the utilization of renewable energy could be forms of reducing the overall environmental impact

(continued)

Table 2.2 (continued)

Source	Water Source, FU, Goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
Friedrrich et al. [69]	Water Source: Groundwater. FU: 1 m^3 of potable water. Goal: compares standard water purification: standard based in flocculation and ozonification and membrane-based filtration, for the reality of South Africa	Cradle-to-gate study, including but without inclusion of membrane manufacture and disposal. Data was obtained from inventory databases. Seven impact categories were evaluated and compared for the process using CML methodology. Gabi software was used to perform the calculations	The study results show that it is not clear which water production process is better according to their environmental impact. The operational stage is responsible for most of the environmental impacts
Biswas [70]	Water source: seawater. FU: 1000 m^3 or potable water. Goal: analysis of a water desalination process in project in Western Australia, that includes microfiltration and reverse osmosis	Cradle-to-gate study in terms of water, not taking into account equipment production and process construction and decommission. Membrane production and replacement is taken into account. Primary data from constructor and suppliers was used. Only one indicator considered: Greenhouse emissions, expressed in terms of carbon equivalents. SimaPro software was used to perform the calculations	Results show that energy production and consumption is main factor controlling the emissions of greenhouse gases. The utilization of renewable can reduce emissions up to 90% when compared with base case study
Bonton et al. [71]	Water source: lake water with a high content of organic matters. FU: 1 m^3 or potable water. Goal: Comparison between of two water treatment plants: one conventional using activated carbon and the other based on nanofiltration	Cradle-to-gate study, taking into account the construction, operation and decommission process plant. Data from two water producing units in Quebex was used. Membrane life cycle considered only partially due to the lack of data. For environmental indicators were assessed using Impact 2002 + methodology. Calculations were performed using SimaPro software	Results show that the environmental impacts depend strongly on the energy source. The process involving nanofiltration is better than the conventional process. The consumption of chemicals is significant from and environmental impact point of view

(continued)

Table 2.2 (continued)

Source	Water Source, FU, Goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
Stokes and Horvath [72]	Water source: river, seawater or recycled water. FU: 123,000 m^3. Goal: compare the environmental impact of producing potable water using three water sources	Cradle-to-grave study, taking into account the entire process, including the construction and decommission phases. Desalination process involves reverse osmosis. Data was obtained from two Californian treatment plants. Six environmental indicators were considered using a software tool, WEST, specifically designed for water treatment systems	Desalination process has the largest environmental impact, showing the importance of the water source when producing potable water. Better option is recycled water. Energy impacts and costs are the dominant factors in the treatment process
Holloway et al. [73]	Water source: used potable water. FU: 1 m^3 of reusable water. Goal: compares two process, one using a membrane bioreactor and the other a reverse osmosis based process	Cradle-to-gate study, taking into account also the construction and decommission phases. Processes were designed using rigorous process simulation and using data from industry and the literature. Energy consumption/carbon emissions were selected was environmental indicators. A specific tool designed to assess water Treatment systems, WWEST, was used	Results show that the operational phase has the largest energy consumption and environmental impact. It is shown also that process optimization can lead to significant reductions on the environmental impact
Jikakli et al. [74]	Water source: Brackish groundwater. FU: 1.25 m^3/d. Goal: Compare the performance of three desalination operating with solar renewable energy, one based on reverse osmosis	Cradle-to-gate study, but construction, decommission, and membrane production were not accounted for. Data was obtained from the EcoInvent inventory database. The Eco-Indicator 99 methodology was used to evaluate 11 environmental indicators. Calculations were made using SimaPro software	Results show that reverse osmosis has the lowest environmental impact. Energy and materials consumption are the most relevant aspects during the operational phase. The key inputs and emissions are identified for each life cycle stage

(continued)

Table 2.2 (continued)

Source	Water Source, FU, Goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
Garfi et al. [75]	Water Source: several. FU: 1 m^3 of potable water. Goal: Compare several options for potable water production and distribution, including one based on reverse osmosis, for Barcelona (Spain) conditions	Cradle-to-gate study. Construction, decommission, and equipment construction and disposal not considered. Domestic and large scale production was considered for each technology, and data from existing water treatment plants was used. Six Environmental indicators were considered, using CML to evaluate the environmental impact. Calculations were performed in the SimaPro software	Results showed that the current traditional system is the best option. For the reverse osmosis small scale production leads to lower environmental impacts, yet large scale production has lower costs
Igos et al. [76]	Source water: river water. FU: 1 m^3 of potable water. Goal: Analyse and identify each are the main hotspots in terms of environmental impacts of existing potable water production systems	Cradle-to-grave study, including construction, equipment, and overall process infrastructure. Data was obtained as much as possible from two French units. ReCiPe and Impact 2002+ were used to evaluate the environmental impact, and calculations were performed SimaPro software	Results show that infrastructure has small environmental impact, mainly resulting from solid deposition and water distribution.. Main impacts are due to energy consumption, for process operation or for activated carbon production
Raluy et al. [77]	Source water: seawater and river water. FU: 25,000 hm^3 (total water transferred). Goal: compare the environmental impact of potable water supply by water desalination, using reverse osmosis, or river water transfer	Results from a previous study on the environmental impact of water desalination technologies [65] by the same authors were used. Three impact assessment methodologies were used: CML, Eco-points, and Eco-Indicator, using SimaPro software to o the calculations. Both primary and secondary data was used	Results support the conclusion that water transfer is the option with lower environmental impact. The operational phase is the dominant life cycle stage, in particular due to energy consumption

(continued)

Table 2.2 (continued)

Source	Water Source, FU, Goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
Vince et al. [78]	Source water: Various sources. FU: 1 m^3 of potable water. Goal: compare the environmental impact of different scenarios for potable water supply, to support the development of decision supporting tool	Cradle-to-grave study, taking into accounting construction, equipment and process infrastructure, but not decommission. Inventory data was obtained from LCI databases. Eight indicators were evaluated using the Impact 2002+ methodology. Calculations and tool development was done using Gabi software	A general analysis of water producing systems concluded that energy generation and consumption has the largest environmental impacts, followed by materials consumption
Ras and Blottnitz [79]	Source water: raw water with known composition. FU: 1000 m^3 of boiler feed water quality. Goal: compare reverse osmosis and ion exchange to reduce water hardness and salinity	Cradle-to-grave study, not considering construction, decommission and equipment. Process data was combined with information from LCI databases. Six environmental indicators were considered using the CML methodology to evaluate the environmental impact. Calculations were performed using SimaPro	Results show that the membrane process option has higher carbon emissions, due to the larger energy consumption, but the remaining environmental impacts are lower. Moreover reverse osmosis generates lower salt waste quantities for disposal
Ribera et al. [80]	Source water: river and groundwater. FU: 1 m^3 of potable water produced. Goal: evaluate the change in environmental impact of implementing nanofiltration in an existing Spanish water treatment plant	Cradle-to-gate study, including construction and equipment, but without decommissioning. Data from real water treatment plants was used, complemented with inventory databases. Twelve environmental indicators were evaluated using the ReCiPe methodology. Calculations were performed using the SimaPro software. S	Several scenarios were studied regarding production capacity and membranes. Results show that increasing water quality also increases the overall environmental impact. A decision supporting tool was developed based on the results

stages considered, membrane processes or technologies considered, data sources, impact evaluation methodologies used, software used if any and main conclusions of the study.

Although the set of selected studies do not represent a full review of the area, they are nonetheless representative of the current state of the art in the area. A comparative analysis of the various studies presented in Table 2.2 allows some conclusions to be drawn. Most of the studies are recent, less than 15 years old, revealing that there is an increasing recognition of LCA as a valuable tool to assess the environmental impact of water production processes [22]. The majority of the works compares different types of technologies, including membranes, with the goal of determining which process or processes have lower environmental impact. Moreover, most of the works presented in Table 2.2 deals with the production of water for human consumption, in particular, desalination processes. For industrial utilization, the application of LCA is much more uncommon. An attributional approach is preferentially used, as the main goal of the LCA studies is to compare the environmental impact a certain quantity of water with a given quality.

Concerning the selected FU, all of the studies considered a certain amount of water produced with wide variations between the values. Also, the source of water can vary significantly between studies, complicating the comparability between studies. While some variation exists in the definition of the system boundaries, the majority of the studies consider the construction of the process units and production systems, and the various production steps from water extraction to water processing, in a cradle-to-gate perspective. However, the production and final disposal of the membranes is seldom taken into account. The water distribution to the final consumer is also rarely considered. As much as possible, data from primary sources is used. The use of LCA software is common to perform the inventory and impact evaluation calculations. Some variability is observed in the selected environmental impacts and methodologies used to evaluate them, making it difficult to compare the results of different studies. The results show that membranes in most situations have better performance in terms of environmental impact when compared with other processes. The impacts due to energy consumption and utilization are the most relevant factors controlling the process environmental impact.

Barjoveanu et al. [81] also performed a comprehensive review of the application of LCA for water treatment systems for human consumption. The authors concluded that most studies consider full treatment systems and compare different technologies, in which membrane systems are a common choice, focusing in particular in the environmental impacts of energy consumption. The study highlights the need to define new impact categories for the economic impacts, and more accurate data. For desalination processes, Gude [82] and Zhou et al. [83] also give a good review of the current state of the art and future research and development trends, focusing on the sustainability of existing and future production. Zhou et al. [83] concluded that much work is still need in the life cycle inventory, in particular, the necessity of using primary data for a proper environmental impact assessment, and more adequate environmental assessment methodologies.

Most studies only considered the LCA methodology as defined by the ISO standards, without any extensions. Nevertheless, it is possible to find some studies that went beyond it. One example is the work of Stokes and Horvath [72] that combine LCA with input and output analysis to assess the costs of the various source water options. The authors concluded that the environmental costs are less than 10% of the overall process costs, and the best option is to use recycled water. Holloway et al. [73] used a consequential LCA approach to compare two options for water treatment, using computational tools to model the processing systems, to understand how the system can be optimized in terms of environmental impact.

Several studies considered process intensification in water treatment for human consumption, for example, combining membrane separation with chemical reaction. Manda et al. [84] studied the potential of using membranes for the removal of micro pollutants from drinking water, in particular, active compounds used in pharmaceutics. An enzyme-coated membrane was compared with a process based in activated carbon using a cradle-to-grave LCA study, considering the production and disposal of the membranes. The FU was 1 m^3 of purified water, data was obtained from the literature and LCI databases, and the environmental impacts were evaluated using the ReCiPe methodology using SimaPro software. The results show that the membrane process is better from an environmental point of view depending on the source of energy and how it is operated, in particular, the frequency in which the membrane is recoated with enzyme.

Lawler et al. [85, 86] examined the life cycle of reverse osmosis membranes used in water desalination processes, including the production and end-of-life options available, a growing problem due to increased production of drinking water from seawater. The authors reviewed the various disposal and regulations applicable, and developed a life cycle model to assess and compare the environmental impact of several end-of-life options. The authors considered as FU a standard membrane module, adequate in this case as their goal is to assess the environmental performance of membranes. Membrane production and disposal was considered and primary data for Australian conditions was used as much as possible. The results show that the characteristics of the membranes have a minimal impact in the environmental impact, and that membrane reuse is better than landfill deposition. The results also show that incineration is also preferable to landfill disposal, even with higher carbon emissions for incineration, but the distance involved should be taken into account in the decision. The study also provides guidelines to help manufacturers and users of reverse osmosis membranes in deciding about the most adequate end-of-life options.

The LCA methodology was also incorporated in modelling and/or optimization tools developed to assist in the design and/or operation of processes for the production of potable water. An example is the work of Vince et al. [78, 87] that looked at the optimization of reverse osmosis based process plants for the production of potable water, combining both economic and environmental aspects. Two environmental indicators were selected, the total recovery rate and the electricity consumption, as they are related to process efficiency and are a measure of the energy consumption, being the last the aspect most relevant for the overall process environmental impact. A FU of 1 m^3 of drinkable was selected and data was obtained from inventory databases. The study concludes that it is possible to design a process that takes into account the trade-offs between costs and environmental impacts, but it is strongly dependent on the local conditions, in particular, availability of renewable power sources.

Mery et al. [88] developed a LCA-based computational tool, EVALEAU, to design and assess the environmental impact of water treatment processes for human consumption. The Umberto LCA software was coupled with a library in which the more relevant processes involved in water treatment systems are described and rigorously modelled. Process data and information from the EcoInvent database were combined to provide a better description of the process consumptions and emissions. A sensitivity toolbox was also implemented to identify process hotspots that represent opportunities for improvement. The tool was applied to a real case study of a water treatment plant in the Paris region, France, and good agreement was observed between simulated values and real data. Ahmadi and Tiruta-Barna [89] included an optimization module in EVALEAU, as a way to tackle the trade-offs between LCA and the economic analysis. The improved tool was used to the case study considered by Mery et al. [88], considering the minimization of environmental impacts (determined using the ReCiPe methodology) and costs and the maximization of water quality.

Loubet et al. [90, 91] developed a tool, WaLA (water system life cycle assessment), to assist in the LCA analysis of urban supply systems. A modular approach was considered, in which each module is a description of a technology (including membrane processes) or process step and/or operation. The tool was implemented in MATLAB/Simulink. The data needed to operate the tool is obtained from the literature, databases or is user input. The WaLA tool was applied to a case study dealing with the water supply in suburban Paris, France. Several future scenarios were compared and the results show that WWT plants have larger environmental impacts when compared to drinking water production and distribution, and the impacts of climate change can be significant in the future.

Beery and Repke [92] analysed the sustainability of various seawater pretreatment methods for reverse osmosis. Both LCA and LCC were used, combined with some selected social factors. A FU of 1 m^3 of potable water produced for a source water with the following characteristics: TDS of 35,000 ppm, temperature of 25 °C. pH equals to 8. The results show that membrane pretreatment is preferable from an economic point view, but less attractive in the environmental and social dimensions. This is due to the higher energy consumption and less flexibility in defining the process characteristics. The authors concluded that more research is needed to improve membrane performance and reduce the environmental impact.

2.3.1.2 Wastewater Treatment

Figure 2.6 presents a generic process system for WWT [93]. It incorporates all the main life cycle stages, in particular, the various types of treatment aimed to deal with specific contaminants. For instance, the biological treatment serves to remove

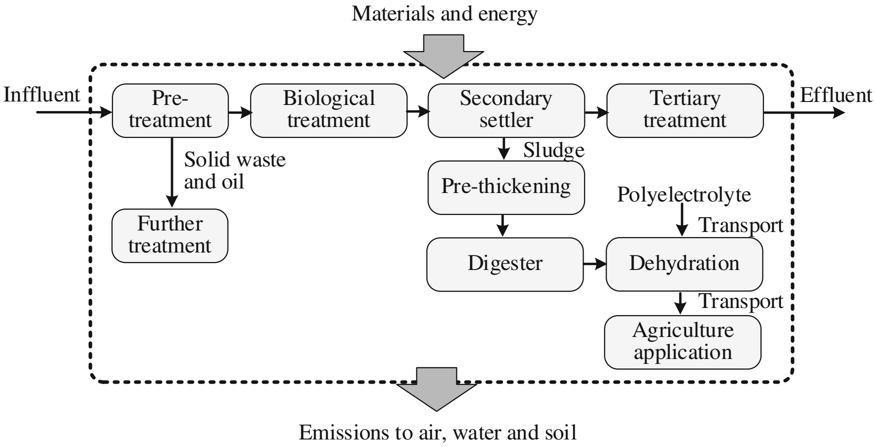

Fig. 2.6 General wastewater treatment process

organic contaminants from wastewater, and in the pretreatment step solids entrained with the wastewater may be removed by filtration. Membrane processes or technologies can be used in the various stages of WWT. When compared to conventional processes, membranes units are more compact, they can achieve higher purification efficiencies, and even in some cases allow the removal of valuable components thus improving the overall process economics [94]. An interesting example is the membrane biological reactors (MBR) that combined membranes with biological treatment, avoiding the need for a downstream filtration to remove biological particles and living cells [95]. The increasingly demanding requirements placed in WWT and the need to recycle and/or reuse water are increasing the attractiveness of membranes processes in WWT. A full description of how membranes can be applied to WWT is outside the scope of this work and can be found elsewhere [94, 96].

As in the case of water production for human or industrial consumption, membranes are used coupled with other process units. Thus from a LCA perspective they have to be considered integrated in the process system. Table 2.3 presents and compares the main features of some LCA studies performed for WWT systems that integrate membrane processes and/or technologies. For each work information is given on the characteristics of the wastewater, FU, goals of the study, system boundaries and life cycle stages considered, membrane processes or technologies considered, data sources, impact evaluation methodologies used, software used if any, and main conclusions of the study.

As in Table 2.2, the set of studies listed in Table 2.3 does not present all available studies in which LCA was applied to the WWT systems that include membrane systems. Nevertheless, the sample of studies can be considered representative, and some conclusions about the current state of the art and potential aspects to be improved can be made. Similar to the situation observed in water

Table 2.3 Comparison of LCA studies for wastewater treatment consumption

Source	Water source, FU, goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
Memon et al. [97]	Source water: greywater of urban households. FU: Variable dependent on water consumption and greywater generation Goal: compares four different treatment processes, including a biological and chemical membrane reactor	Construction and process operation are considered, assuming for design purposes that system will serve 500 households. Energy and materials consumption are accounted for. Data was obtained from suppliers and simulation results. Ten environmental impact categories were considered, using CML and Eco-Indicator as evaluation methodologies. Calculations were performed using SimaPro software	Processes based on natural processes have the lowest environmental impacts. Amid membranes is the chemical membrane which has the worst performance. Utilization step is dominant for all technologies. A tool for greywater treatment process selection was developed
Ortiz et al. [98]	Source water: urban wastewater from a small Spanish city with a population of 13,200. FU: 3000 m^3/day or treated water. Goal: Compare three process variants: without membranes, with ultra filtration, or with a MBR	Construction, membrane replacement each seven years, and process operation are taken into account. Data was obtained from an existing wastewater treatment from a small Spanish town. Five environmental impact categories were considered, using CML 2 baseline 2000, Eco-Points 97 and Eco-Indicator 99—as assessment methods. Calculations were performed in SimaPro software	Results show that the process operation has the largest environmental impact. The inclusion of the membrane process increases the environmental impact when compared with conventional process, but better final water quality justify their inclusion

(continued)

Table 2.3 (continued)

Source	Water source, FU, goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
Coday et al. [99]	Source water: wastewater resulting from shale oil extraction. FU: 1 barrel of wastewater generated. Goal: compare two forward osmosis treatment process for water recover: standalone or a complete osmotic dilution system; with transportation and well injection for water disposal	Cradle-to-gate study, including construction and equipment, for the membrane-based processes, and gate to gate for transportation and well disposal. Data was obtained from the literature and from the USA Input-Output 2002 database. Calculations were performed in the SimaPro LCA software, for ten environmental impact categories, and using TRACI as evaluation methodology	Energy demand is main contributor in the membrane-based processes for the overall environmental impact. Results show that the environmental impacts of the three processes are similar, but membranes can reduce significantly pit water management costs and the need of wastewater transportation
Remy and Jekel [100]	Source water: wastewater from a small town of 5000. FU: not specified but takes into account human needs. Goal: energy analysis of various processes, including a MBR	Cradle-to-gate study, considering construction of infrastructure but not equipment. Data was based on information from a real wastewater process in Germany, coupled from information from databases for the materials used. The cumulative energy demand was the one indicator evaluated. Calculations were performed using Umberto software	Process operation and materials require similar amounts of energy. Anaerobic digestion only reduces slightly the energy needs. System involving the MBR has the worst performance in terms of energy consumption
Remy et al. [101]	Source water: wastewater with a COD of 120. FU: defined as population equivalent per year, for a total of 87.6 million m^3/year. Goal: compare several technologies for	Cradle-to-gate study, including construction and operation. Ultrafiltration and filtration with a ceramic membrane were considered. Data was obtained from a real life wastewater	Results show that water quality in processes involving membranes is higher, but with larger energy and materials consumption. Non membrane processes are able to fulfil

(continued)

Table 2.3 (continued)

Source	Water source, FU, goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
	tertiary water treatment in a wastewater treatment plant in Berlin	plant and inventory databases. Energy cumulative consumption and six environmental indicators evaluated using the ReCiPe 2008 were selected. Calculations were performed using Umberto software	requirements, making membranes processes non competitive
Kobayashi et al. [102]	Source water: urban wastewater from an Australian city. FU: 18×10^6 m^3/year. Goal: compare the environmental impact and risk for the human health of recycling wastewater for human consumption, involving reverse osmosis	Work combines LCA and quantitative microbial risk assessment. Construction and final disposal, as well equipment, are not take into account. Primary data was complemented with data gathered in databases. Six indicators were considered using ReCiPe for their evaluation. Calculation were performed using Gabi 6 software	Energy consumption in the membrane process is the most relevant issue in terms of impact. Although recycling water increases impact, water quality is improved. Also, the usage of renewable energy reduces the overall environmental impact
O'Connor et al. [103]	Source water: pulp and paper industrial wastewater with high COD and organic halides. FU: 100 m^3 of recycled water for irrigation. Goal: compare four treatment alternatives, including reverse osmosis and ultrafiltration	Cradle-to-gate study, excluding decommissioning but including construction whenever data was available. Process calculation performed using Matlab using information from the literature. Four indicators were considered using CML as impact evaluation methodology. Calculations were performed using SimaPro	Energy consumption increases with treatment intensity. Yet, carbon emissions can be controlled through and adequate sludge disposal. Process configurations have the largest energy consumption

(continued)

Table 2.3 (continued)

Source	Water source, FU, goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
Pintilie et al. [104]	Source water: urban wastewater from Tarragona, Spain. FU: 1 m^3 entering wastewater treatment plant. Goal: compare the impact of having or not tertiary water treatment, which includes a reverse osmosis process, in potential water reuse	Only operational activities were considered. Primary data is obtained from a real wastewater treatment plant, complemented with information from databases. Ten environmental impacts were assessed using ReCiPe methodology. Energy cumulative demand was assessed using the CML methodology. Calculations were performed in unspecified LCA software	Tertiary treatment increases the environmental impact, in particular due to the increase in energy consumption. Water quality improvement may be relevant depending on the local water resources, and utilization of renewable energy may reduce significantly environmental impacts
Pirani et al. [105]	Source water: wastewater generated in Masdar City, Abu Dhabi. FU: 1 m^3 of treated water. Goal: compare two technologies for wastewater treatment: a conventional activated sludge reactor and a MBR	Cradle to gate but without the construction and decommission of process units. Membrane construction was considered. Data from inventory databases and literature was used. The Eco-Indicator 99 was used to evaluate the environmental impacts. Calculations were done using the SimaPro software	MBR has lower environmental impacts when compared with the conventional activated sludge process. However, energy consumption is high. MBR is better used in a decentralized way
Vlasopoulos et al. [106]	Source water: wastewater originated in oil and/or gas extraction processes. FU: 10,000 m^3 of wastewater processed for 15 years. Goal: Compare several treatment technologies, with the goal of reusing	Cradle-to-grave study, considering construction of process system and units. An extensive analysis of the potential process combinations was done. Primary data from constructors and process units suppliers	For most technologies, including membranes, the environmental impacts result mainly from the operation phase, in particular due to the energy consumption. The results show that for this type of waste water

(continued)

Table 2.3 (continued)

Source	Water source, FU, goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
	treated water for agricultural purposes	was used as much as possible. Five environmental indicators were considered using the CML evaluation methodology. Calculation were done using SimaPro software	micro filtration is a good choice
Rahman et al. [107]	Source water: urban wastewater for average US conditions. FU: 1 m^3 of incoming wastewater. Goal: compare several advanced removal processes for nutrient removal, especially N and P, including membrane processes	Cradle-to-grave study, considering construction and process operation. Three levels of treatment are studied considering different treatment process configurations. Inventory data was obtained using process simulation combined with databases. Five environmental indicators were quantified using TRACI as evaluation methodology Calculations were performed in SimaPro software	Results show that more efficient technologies, including membranes, reduce the environmental impact, at the expense of larger energy and chemicals consumption. Inclusion of tertiary treatment may not be adequated due to the increase in the overall environmental impact
Høibye et al. [108]	Source water: wastewater generated under Danish conditions. FU: 1 m^3 of treated wastewater. Goal: compare FIVE treatment technologies, including a MBR, considering technical, economic and environmental aspects	Only process operation was considered in the process system. Data was obtained from the literature and inventory databases. Environmental impact assessment was performed considering several contaminants and four indicators, evaluated suing the EDIP methodology. No specific software was used in the calculations	The results show by using a MBR larger environmental impacts will result, due to larger energy consumption, but with an improved water quality. The best process depends ultimately on the desired water quality

(continued)

Table 2.3 (continued)

Source	Water source, FU, goal	System boundaries, membrane technologies and impact evaluation	Main study conclusions
Garcia-Montoya et al. [109]	Source water: wastewater with a COD of 900 g/m^3. FU = One person Equivalent per year. Goal: Compare several forms of water reuse, including wastewater treatment based on a membrane bioreactor, for a case study of the Mexican city of Morelia	Only the operational and maintenance activities are considered. Inventory data is obtained from Mexican wastewater treatment plants and from process simulators (Aspen-Hysis). Seven environmental indicators were evaluated using IMPAC 2002 + methodology. No specific software was used in the calculations	Results show that higher final water quality is obtained in the scenarios involving the membrane bioreactor, at the expense of higher energy consumption and overall environmental impact. The study shows that it is possible to fulfil fresh water needs while minimizing the environmental impact
Machado et al. [110]	Source water: wastewater with a COD of 900 g/m^3. FU = one person equivalent per year. Goal: compare three wastewater treatment processes aimed for small and decentralized communities, including one that use a geotextile membrane	Cradle-to-gate study, construction and maintenance was taken into account. Inventory data was obtained from the literature and inventory databases. Six environmental indicators, including energy consumption, were evaluated using the CML methodology. Calculations were performed in SimaPro software	Results show that systems design for low energy consumption, including the geotextile membrane, have lower energy and environmental impact. Several proposals to improve the environmental performance were proposed and evaluated

treatment systems for human/industrial consumption, most of studies are less than 15 years old, following the trend observed in the last two decades of the increase importance given to LCA as one of main tools to assess the environmental impact of systems, either products and processes [22]. Most works analyse complete WWT systems that include membranes processes performing specific tasks, usually in tertiary treatment. As in Table 2.2, the comparison between various technologies, among which membranes, in terms of environmental impact is one of the main goals of the studies. Wastewater of various origins and characteristics are considered in the studies, resulting in significant variations inter studies in the FU defined. Most of the studies take into account all water processing stages, construction of infrastructure and equipment, but the final disposal/distribution and membrane production are seldom considered. As much as possible primary data was used, in particular, from real operating WWT plants, complemented whenever necessary with data from LCI databases. The use of LCA software is common, both to perform and/or complement the data inventory and to carry out the assessment of the environmental impacts. Significant variability is observed in the environmental impacts quantified and the methodologies used to assess them, even though energy consumption and greenhouse gases emissions are normally considered. Combined with the variability in the FU and wastewater sources, this situation makes the comparison between studies complex if not impossible. The results show that the utilization of membranes normally results in better processed water quality, but at the expense of larger energy and chemicals consumption. The impacts due to energy consumption and utilization are the most relevant factors controlling the process environmental impact

Barjoveanu et al. [81] and Coriminas et al. [111] also reviewed the state of the art concerning the application of LCA to WWT systems. The authors concluded that it is clear that LCA is a valuable tool to improve the environmental performance of WWT systems, and practitioners are increasingly aware and interested in the methodology. The analysis of the literature also shows that there is some variability between studies, in particular in definition of the FU, system boundary, impact categories and calculation methods. A need to develop standard guidelines to apply LCA in WWT is identified, to ensure the quality, reproducibility and comparability of studies in the area.

Most of the studies presented in Table 2.3 used on the standard methodology, as described in the ISO standard. To the author's knowledge, no works exist in the open literature in the consequential LCA framework or S-LCA was applied to WWT systems involving membrane processes or technologies. Concerning LCC, Life Cycle Costing, some examples can be found in which the methodology was used coupled with LCA. Coday et al. [99] have applied LCC in their cases study, taking into account the costs of all the treatment stages of both technologies. The authors concluded that the forward osmosis treatment is significantly cheaper than the standard procedure of deep well disposal. Garcia-Montoya [109] consider the operational costs in their analysis of WWT for residential consumption, having demonstrated that it is possible to simultaneously optimize the overall environmental impact and the costs of running such systems.

Table 2.3 only lists studies in which full WWT systems that integrate membrane technologies are considered. From a practical point of view, this approach allows the comparison of different treatment, but does not allow a detailed analysis of the membrane systems and has their performance depends on the other parts. Yet, it is possible to found in the literature LCA studies in which the study scope is the membrane process alone not coupled with other processes. An example is the work of Hospido et al. [112] that compared four types of membrane reactors used for WWT with different configurations and complexities. The production of the membrane units was taken into account. A FU of 1 m^3 of permeated produced was used, and data was obtained from inventory databases. The analysis showed that energy consumption and sludge disposal have the most relevant environmental impacts, and increasing complexity increases the operational costs. Ioannou-Tofta et al. [113] also analysed a membrane bioreactor for the treatment of urban wastewater, and obtained similar conclusions concerning energy consumption, but also concluded that the materials used in the materials are also relevant to the overall environmental impact. The authors also concluded that the characteristics of energy mix are also relevant.

Bayer et al. [114] performed a LCA study of a combined membrane and liquid–liquid reactive extraction process for the removal of phenolic compounds from wastewater. Because it is a new technology, the main work goals are the identification of the optimal equipment sizes and operational conditions. The treatment process was modelled using MATLAB and the environmental impacts were evaluated using the Gabi software. Tangsubkul et al. [115] examined the influence of the operating conditions in the environmental performance of microfiltration processes used in WWT plants. Several options for the chemical cleaning of the membranes were considered. The FU is 1000 m^3 of wastewater, and seven environmental indicators were evaluated using equivalency factors adequate for Australian conditions. The results show that the lowest environmental impacts occur for low flux and high transmembrane pressure, and the choice of the cleaning chemicals can have a significant impact.

Razali et al. [116] analysed the environmental impact of the wastewater generated in membrane production, which can be a significant problem. Although the authors did not perform an LCA study, the results are relevant from a life cycle perspective as they can be used to select the most adequate WWT technology for membrane production processes. Several types of adsorbents were experimentally studied, and the results show that it is possible to treat the water for reuse in the membrane production process, significantly reducing the water needs for the process.

The sustainability of water treatment processes was also considered in the literature. Normally, the membrane is included in the process and not analysed in detail. An exception is the works of Pretel et al. [117, 118] that studied the environmental and economic sustainability of submerged anaerobic membrane reactor for treating urban wastewater. The analysis combined simulation of steady-state performance with LCA and LCC. A comparison with commonly used WWT methods was done. Results show that the membrane reactor significantly reduces the overall process's operational costs and environmental impacts.

Balkema et al. [119], Kalbar et al. [120], and Plakas et al. [121] proposed several methodologies to assess the sustainability of WWT systems based on different technologies. The indicators are selected based on their use in practice, and are calculated whenever possible based on the life cycle of the treatment system. The frameworks are intended for use in any process, including those with membrane systems. Kalbar et al. [120] and Plakas et al. [121] also proposed an aggregation scheme based on the application of weighting factors to the several indicators, to facilitate the ranking of the various technologies and decision-making.

Chen et al. [122] performed a critical review of the sustainability of recycling water schemes, including the WWT process. Several environmental assessment tools were reviewed including LCA, and their strengths and weakness were evaluated. The authors concluded that when LCA is used to select WWT technologies a better assessment of the overall process sustainability is performed.

2.3.2 Other Applications

For other processes besides water processing systems, in which membranes are key part of the system, the application of LCA has been limited. However, some LCA studies can be found in the literature in various areas besides water treatment. Some of them are described below by area of application.

2.3.2.1 Food Processing

Food processing is an area where membranes are used extensively, and where LCA is being used increasingly. For example, Omont et al. [123, 124] compared the environmental impact of two milk protein separation processes: chromatography and membrane filtration (micro- and ultrafiltration). The raw material is whey generated as a waste from normal dairy processes, considering all processes needed to obtain the final product. A FU corresponding to the daily quantity of milk processed in a French dairy (583 m^3). Environmental impacts were assessed using the IMPACT 2002+ methodology and SimaPro software for the calculations. The comparison results show that the membrane process is somewhat better than the chromatographic process, in particular, in the human and resources impact categories.

Aldaco et al. [125] and Margallo et al. [126] considered the partial dealcoholization of wines, comparing the environmental performance of several membrane-based technologies using the LCA methodology. A cradle-to-gate study was done, for a FU of 1 m^3 of dealcoholized wine. The studies concluded that reverse osmosis has high consumption of energy and may damage the wine quality, having the authors propose a new membrane technology that reduces those problems. Moreover, the normally used processes also have higher resources consumption, and the ability to valorize the wastewater generated is important in the overall system sustainability. Notarnicola et al. [127] applied the LCA methodology to a grape must concentration used to minimize the natural raw materials variability in a southern Italy winery. The process is based on reverse osmosis and the analysis uses primary data from industrial practice. A FU of 1 m^3 of wine (Rose Bombino) with a alcoholic degree increased from 10.5 to 11.5 was considered. Data was obtained from inventory databases. Eleven environmental indicators were evaluated using the CML methodology. The study concluded that energy consumption and membrane cleaning are the main operations in terms of environmental impacts. From the data, it was possible to identify the operational conditions for which the environmental impact is minimized and propose improvements to ensure that.

2.3.2.2 Gas Processing

Adbel-Salam and Simonson [128] considered a novel system to reduce the air humidity in air conditioning systems based on a membrane that isolates the desiccant and allows the removal of the water. Although the article does not present the results of an LCA study, the energy consumption and life cycle costs of the proposed system were compared with conventional systems, showing improvements in both aspects.

Gas separation is another area where membranes are also extensively used in various contexts. Cuéllar-Franca and Azapagic [129] performed a critical analysis of the state of the art on the available technologies for carbon capture, storage and utilization. Membranes are a good option capture CO_2, and depending on the impact category they are better than other options. The comparison between the various studies shows that significant reductions in the greenhouse gases emissions from power plants more than 50% are achievable. However, for other environmental indicators the sequestration can actually aggravate their values. The energy consumption is a disadvantage for membranes technologies that show correspondingly the higher global warming potentials.

Zhang et al. [130] compared three post-combustion carbon capture technologies, including a membrane system and a hybrid membrane-cryogenic process, from an energetic and life cycle perspectives. The performance of the capture systems was assessed by simulation. The results show that the membrane processes, and in particular the hybrid systems, have lower energy consumption and environmental impacts when compared with solvent-based processes, in particular, based in MEA absorption. Also, Schreiber et al. [131] and Troy et al. [132] compared various technologies for carbon capture using LCA, having also concluded that membranes have the best environmental performance. Both works considered the production of the membranes and supporting equipment, having explored scenarios for power plant operation and CO_2 generation. Petrakopoulou et al. [133] used LCA to compare two processes for pre-combustion CO_2 capture: one a standard methane steam reformer and the other a catalytic membrane used to remove the hydrogen from the natural gas. The results show that both processes have similar environmental impacts and both have to be improved in terms of efficiency to be viable options to be included in existing power plants.

2.3.2.3 Sustainability Evaluation

LCA methodology is currently seen as the most adequate framework to assess the sustainability of a product or process [134–136]. Most of the environmental indicators defined in a LCA study can be used as sustainability indicators, and the inventory analysis process and the impact assessment methodologies are also relevant. Thus, LCA is also applied to assess the sustainability of membrane systems, aiming to identify hotspots and improve their sustainability performance.

One example is the article by Szekely et al. [137], in which the sustainability of organic solvent nanofiltration is assessed based on a LCT perspective. The authors analysed all the steps of the membrane process, starting with the production of the membranes, process operation and end-of-life options for the membranes and other process units. Energy consumption, carbon footprint and operational parameters were the main indicators used in the evaluation. The various options and process characteristics, in each life cycle stage are compared with each other based on an extensive analysis of the literature in order to determine which ones are better and which operating conditions are desirable.

Criscuoli and Drioli [138], and Brunetti et al. [139] analysed the utilization of membrane processes to increase the sustainability of industrial process, in particular, in the water and gas treatment when compared with other options also used in industrial practice. Although the sustainability evaluation is not directly based on an LCT approach, some of the indicators are calculated taking into account the overall system and its performance. The indicator's main goal is to account for process intensification due to utilization of membranes, when compared with other processes, and serve as a decision-making instrument in the retrofitting of existing or new units and/or processes for which membranes may be viable option. Pal and Nayak [140] used a similar but simpler approach in the analysis of a membrane process for the production of acetic acid from waste cheese whey. The analysis focused on the process operation and was restricted to the equipment costs, operational and energy expenses.

2.4 Conclusions

This chapter presented a description of the principal principles of the LCA methodology, and how it has been applied to systems where membrane units are at the core of process or perform significant tasks, with a focus in water processing systems, either for human/industrial consumption or for WWT. As stated above, membranes are already extensively used in various processes and production systems. It is expected that the range of applications will increase in future, due the strong investment in research and development in the area, and the general belief that membrane systems are usually more sustainable [4]. Still, when designing and/or using membrane processes in practice is essential to support decisions based on the results of quantitative and objective tools, of which LCA methodology is currently the methodology of choice to evaluate the environmental impact of products/services or processes.

However, the analysis of the open literature shows that the application of LCA for evaluating membrane processes is still limited. This situation is odd as membranes are many times promoted as better options from an environmental point of view when compared with other processes and/or technologies. However, recent years have witnessed a growing interest in the application of LCA to evaluate membrane systems and/or technologies, as shown by the increasing number of works published in the last few years.

Some aspects that should be consider in future LCA studies of the systems involving membranes include:

- The manufacture and preparation of the membranes and/or corresponding modules should be considered more in detail and explicitly.
- The studies should take into account explicitly the membrane module maintenance and final disposal/recycling.
- More studies dealing with the sustainability of membrane systems are needed. Very few studies deal with the economic and social impacts of using this type of technologies. Also, many sustainability assessments are not based on a LCT approach.
- Care should be given to the selection of the FU and the environmental impact categories to be evaluated, in order to ensure comparisons as objective as possible between different studies.
- More Consequential LCA studies should be performed. As in many processes membranes will replace already existing processes or systems, its feasibility in terms of environmental impacts must take into account the existence of other technologies that perform the same tasks.

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Chapter 3
Process Intensification: Definition and Application to Membrane Processes

Andrzej Benedykt Koltuniewicz

Abstract The main ways of intensification of membrane processes were classified into three groups. In the first group those methods, which depend on the selection of the type of the membrane in terms of material and microstructure, were described. The second group includes information relating to concentration polarization, which is always present in membrane separation processes. In practice, the occurrence of concentration polarization exerts even more distinct effect than resistance of the membrane itself with respect to performance. Reduction of the concentration polarization allows greater permeate flux but requires additional actions and additional energy. The third way of the intensification of membrane processes is to design a suitable configuration, i.e., the selection of membrane modules and their connections. The most spectacular way of process intensification of separation is the use of modern hybrid processes, which are discussed later in this chapter.

Keywords Process intensification · Membrane properties · Concentration polarization · Plant configuration · Membrane-based hybrid processes

List of Symbols

A	Surface area [m^2]
A	Accumulation at Eqs. 3.19 and 3.20 [s^{-1}]
C	Concentration [kg m^{-3}]
CF	Concentration factor (CF = C_R/C_F) [−]
D	Diffusion coefficient [m^2 s^{-1}]
d	Diameter [m]
f	Age function [–]

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J	Volumetric permeate flux [m^{3} m^{-2}s^{-1}]
J_i	Mass permeate flux for ith component [kg m^{-2} s^{-1}]
$J(t)$	Instantaneous flux [m^{3} m^{-2} s^{-1}]
j	By-pass ratio ($j = m_b/m_F$) [−]
K	Permeability factor [kg m^{-1} s^{-1} bar^{-1}]
k	Boltzmann constant (1.38064852 × 10^{-23}) [m^{2} kg s^{-2} K^{-1}]
k	Constant in Hermia's Eq. 3.3. [−]
k	Mass transport coefficient (overall) [m/s]
l	Thickness of the membrane [m]
M	Molecular mass [kg/kmol]
m	Mass flow rate [kg/s]
m	The ratio of dry mass to the wet mass [−]
n	Constant in Hermia's equation Eq. 3.21 [−]
n	Circulation ratio ($n = m_c/m_R$) [−]
P	Pressure [bar]
Q	Volumetric flow rate [m^{3} s^{-1}]
R	Universal gas constant (8.314459848) [J K^{-1} mol^{-1}]
R	Volumetric flow resistance [bar s m^{-1}]
r	Pore radius [m]
R	Retention coefficient [−]
RC	Recovery factor (RC = m$_{P}$/m$_{F}$) [–]
Re	Reynolds number (Re = $ud\rho/\mu$) [−]
S	Solubility factor ($S = \Delta C/\Delta P$) [kg m^{-3} bar]
s	Rate of surface renewal (by Danckwerts) [m s^{-1}]
Sh	Sherwood number ($Sh = k\ d/D$) [−]
Sc	Schmidt number ($Sc = \mu/D\rho$) [−]
T	Temperature [K]
t	Time [s]
U	Electrical potential [V]
u	Velocity [m s^{-1}]
V	Volume [m^{3}]

Greek Symbols

α	Specific resistance of the cake [−]
γ	Shear rate [s^{-1}]
δ	Thickness of the boundary layer [m]
η	Viscosity [kg m^{-1} s^{-1}]
ϕ	Solid fraction in suspension [−]
λ	Mean free path of molecules [m]
μ	Chemical potential [J mol^{-1}]
π	Osmotic pressure [bar]
ρ	Density [kg m^{-3}]
ψ	The shape constant [-]

Subscripts

A	Component A
crit	Critical (flux)
c	Cleaning (time)
drag	Drag (force)
F	Feed
G	Gel
lift	Lifting (force)
p	Process (time)
P	Permeate
R	Retentate
W	Wall

3.1 Introduction

In the light of various definitions, the term “process intensification” may be summarized to be synonymous with the rationalization of the processes. Depending on the specific objective of process intensification, it may refer to the reduction of the size of the equipment, the reduction of the consumption of energy and raw materials, as well as reduction of emissions of pollutants. In any case, this is a way to improve the efficiency of the process and consequently reduce the cost of the entire production and even to bring a series of various benefits for sustainable development. In this aspect, however, it may be a contradiction between the intensification of production and sustainable development. Such a narrow understanding of intensification as production growth can also lead to increased consumption of nonrenewable resources, increased energy consumption, and global emissions and unemployment even when using very efficient and profitable technologies, which is in opposition to the sustainable development. Therefore, the broader term of sustainable development should not be overused in the context of process intensification. However, in most cases, the “process intensification” leads to better utilization of raw materials, energy, and equipment and eventually also the human potential. There are various opinions concerning the definitions of process intensification. Some of the most cited ones are shown below:

- Process intensification as a strategy for making dramatic reductions in the size of a chemical plant so as to reach a given production objective [1].
- Process intensification significantly improves the transport rates, it gives every molecules the same process experience. It could be achieved through improved control of reactor kinetics giving the higher selectivity/reduced wastes products, higher energy efficiency, reduced capital costs, and reduced inventory/improved intrinsic safety [2].

- Any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology is process intensification! [3]
- Process intensification is the strategy of making significant reductions in the size of a chemical plant in order to achieve a given production objective. Innovations in catalytic reactors, which constitute the heart of such process technologies, are often the preferred starting point [4].
- Process intensification has emerged as a promising field which can effectively tackle the challenges of significant process enhancement, whilst also offering the potential to diminish the environmental impact presented by the chemical industry [5].
- Process intensification (PI) is potential for process improvement, to meet the increasing demands for sustainable production [6].
- Process intensification performed in terms of the following ratios: productivity/size; productivity/weight; flexibility; and modularity [7].
- Process intensification is the process for improving profitability and remaining competitive [8].

It should be noted that various membrane processes are currently at different stages of development and require different approaches with respect to intensification. Some of them (like reverse osmosis) have already reached commercial maturity long ago allowing their robust and reliable use. The other processes (as membrane distillation) were very promising for a long time; however, they have never been applied in commercial practice due to unresolved numerous technical problems. The membrane processes are particularly suitable for intensification of the separation processes, which can be developed as clean technologies because they do not produce any waste and contribute to reducing the consumption of materials and energy [9]. Clean Technologies were introduced as "any technical measures taken at various industries to reduce or even eliminate at source the production of any nuisance, pollution, or waste, and to help saving raw materials, natural resources and energy" by EU Commission [10, 11]. Clean technologies are based on separation processes for the removal, recovery, reuse, or recycling of various substances and material streams. Main attributes of clean technologies are reduction of the wastes at source, conservation and rational use of raw materials, conservation and rational use of energy, and optimization of production processes. With the help of membranes, nowadays the various substances from wastewaters, mine water, and leachates can be recovered, such as water, unreacted substrates, catalysts, solvents, surfactants, detergents, adsorbents, cooling agents, metal ions, heavy metals, organic compounds, dyes, finishing agents, and process liquids (including bleaching tannery solutions, acids, and salts from pickling and galvanic baths). This reduces the consumption of raw materials in different industries and simultaneously helps to reduce emissions in a sustainable way.

The membranes contribute to the protection and rational use of energy which is also a way of process intensification. The energy savings may be achieved directly through the use of less energy-intensive membrane processes instead of conventional thermal processes used for example during the drying and distillation that are less efficient. The membrane processes use many different systems, which result in a reduction in the cost of separation. During ultrafiltration and microfiltration, the energy consumption may be reduced by the use of submerged membranes (under aeration) instead of expensive recirculation of retentate in a cross-flow mode. In the reverse osmosis more than half of the energy of pressure may be recovered by the use of so-called boosters. The very spectacular effects of intensification are achieved by the use of hybrid processes that are the combinations of several different unit processes which functionally play the same role (as separation or chemical reaction), but in a different way. The membranes form a plurality of such hybrids that lead to the best solutions of separation techniques, like for instance a combination distillation pervaporation for easy separation of azeotropes. During membrane distillation the small temperature differences may be used (so-called "waste heat") for the separation of volatile substances from wastewater. It is very common to use the hybrid processes as a combination of membrane processes with various unit processes for the removal of water prior to drying of milk, egg protein, coffee, tea, cocoa, and other food products of the "instant" type. The extremely expensive chromatography process of separation in the pressure columns can be replaced by the much cheaper membrane chromatography process. In this case, the sizes of membrane pores are matched to the size of ligands, so enhance the collisions between molecules more efficiently than inside of packed chromatography columns. There are many hybrid systems, but so far there is no systematically developed knowledge on the subject. So, a further development in this area is spontaneous and depends solely on the creativity and intuition of the inventors. Some attempts to systematize and classify membrane-based hybrid systems are presented later in this chapter. In certain membrane processes, e.g., pervaporation and membrane distillation, also the heat is recovered in addition to the mass.

Despite the many advantages of the membranes, they are usually very sensitive to many different stresses, which limit their use in industrial practice [9, 26]. Drawbacks of the membranes include weak mechanical strength, chemical incompatibility with respect to certain ingredients, or heat sensitivity of some membrane materials. As a result of improper selection of membranes for the given process, a serious reduction of membrane life can be expected. After making the proper choice of the membrane, a new problem appears, i.e., the need to reduce the concentration polarization, which always occurs during the separation of substances. The concentration polarization is the occurrence of the boundary layer which is formed by the retention of the substance on the membrane. The concentration polarization is always the cause of decrease in the permeate flux, and permanent loss of permeability due to subsequent fouling which is ever the inseparable phenomenon. Therefore, when designing a membrane installation, a compromise between operating costs for energy consumption and maintenance, as well as the capital costs of membranes and other devices (e.g., CIP), has to be properly optimized. The proper selection of the membrane modules and the type of the media occurring in the process should also be taken into account. The criteria for this choice must be the costs, which depend mainly on how to reduce the concentration polarization and fouling, how to select the membrane, the proper type of module, the corresponding hydraulic conditions, and the other parameters (such as pressure, temperature, pH, etc.). The method and frequency of the membranes cleaning, automation, type of maintenance, plant size, and membrane replacement, etc. (see Tables 3.1 and 3.2) should be duly optimized. A very important way of intensification of membrane processes is the appropriate use of multistage systems. In this case, the various connections of membrane modules are used to improve the quality and quantity of the main products, i.e., the retentate or permeate. The volumetric permeate flux (*J*) is the most commonly used parameter for intensification of membrane processes, which expresses the flow rate of the product transported through the surface of the membrane.

$$J_{\mathrm{A}} = \frac{1}{A} \cdot \frac{\mathrm{d}V}{\mathrm{d}t} \quad \left[\frac{\mathrm{m}^3}{\mathrm{m}^2\ \mathrm{s}}\right]. \tag{3.1}$$

The required membrane surface area for the assumed flow rate can be calculated on the basis of the permeate flux (*J*). It should be emphasized that the surface of the membrane A is also the basic factor for determining the components of the operating cost (see Table 3.1) and capital costs (Table 3.2) for all the membrane processes. Thus, all the cost components of the membrane process can be calculated based on the actual permeate flux, which can be achieved for any given type of membrane and conditions. It is therefore important to determine accurately the permeate stream and its stability over the longest possible time (the lifetime of membranes).

The particular ways of intensification of membrane processes are discussed as follows:

(i) Control of mass transport mechanisms inside membranes and appropriate choice of membrane;
(ii) Control of the performance and mass transport mechanisms at membrane boundary layers for reducing polarization phenomena, and appropriate choice of membrane modules;
(iii) The designing of the efficient membrane installations by combining membrane modules in multistage membrane systems; and

Table 3.1 Capital-cost components in large UF/MF Plants

Capital cost components	Range of components in Large UF/MF plants
Energy consumption	0.5–5 kWh/m^3 permeated
Cleaning chemicals and lost products	\$10–100/m^2 membrane installed-year
Membrane replacement	1–5 years at \$20–40 m^2; 10–20 years at \$200/m^2
Operating, cleaning, and maintenance labor	2–3% of installed capital
Maintenance materials	0.6–0.006% of installed capital

Table 3.2 Operating-cost range for large UF/MF Plants

Investment cost components	Share of the total cost %
Membranes and membrane housings	17–40
Pumps, motor, etc.	15–9
Pipes, valves, and framework	35–31
Cleaning system	18–10
Control panel	15–10

(iv) The integration of membrane processes with other unit processes for efficient hybrid processes.

During the intensification of the membrane processes, the total costs within the assumed period of time should be taken into account. Therefore, efforts incurred to increase the permeate flux must take into account all the components of the costs that may arise in the system.

All costs of membrane processes usually refer to the size of the system, mainly to the total surface area of the membranes installed that mainly depends on the actual permeate flux. Serious share of the cost around 30% is consumed by installation, piping, valves, pumps and motors, and control panels and automation (10–15%). In the case of the need for automatic cleaning of the membranes, the further expense (10–20%) should be expected. The expected energy consumption for such systems is at a level of 0.5–5 kWh/m^3 permeate. The annual cost of chemical cleaning and lost products are estimated to be \$10–100/m^2, depending on the surface area of the membranes. The membranes must be exchanged depending on the working conditions and on their quality. Cheaper membranes need to be replaced in shorter periods of time every 1–5 years, and the cost is about \$20–40/m^2. The more expensive membranes can be even exploited for a prolonged period of 10–20 years, but their price is expected to be around \$200. The maintenance costs, including operating costs, and cleaning cost at the level of 2–3% of the cost of capital should also be taken into consideration.

3.2 Intensification of Processes Through Appropriate Choice of Membranes

Membranes are used in a variety of sectors of industries due to their high separation efficiency and the moderate cost. However, to fully explore all the advantages of the membranes, it should be noted that they are very sensitive to many different stresses. Therefore, the appropriate choice of material and structure of the membranes is the prerequisite for correct and long-term operation of any given membrane process. The low mechanical strength and high sensitivity for temperature and pressure are the most common physical stresses of membranes. Also the chemical compatibility of the membrane material with all the components of the feed has to be carefully checked in the entire range of temperature, pH, and concentrations. The biological factors may also exert unwanted effects on membrane material in some conditions. Proper selection of the membrane structure and adjusting the pore size of the membrane to the size of the separated particles is possible in some cases. The separated particles should not penetrate deeper into the membrane pores, but should be collected only on the membrane surface. Then they can be easily removed without changing the intrinsic membrane resistance and other properties. The idea of asymmetric membranes was probably the most important event for the commercialization of membranes in the 70s. Since then the many innovations were introduced to membrane technologies such as the use of double asymmetry (on the inside and outside), the introduction of multilayer composite membranes. The most effective way to increase the efficiency of the membranes is the preparation of membranes with a uniform pore size adjusted to the given system. Laser lithography methods [12] can be very helpful in the preparation of membranes with a precisely defined pore size and a very high share of the pore area to the membrane surface area (Fig. 3.1). This will allow obtaining the high selectivity and the high permeability simultaneously.

In 2003, Peter Agree and Roderick MacKinnon received the Nobel Prize for discoveries concerning channels in the cell membrane. AQP1 aquaporin can transport approximately 3 trillion water molecules within seconds [13]. Intensive studies are currently performed toward the use of this discovery in the production of innovative membranes, which may soon revolutionize the technique of separation. The single-file diffusion without intermolecular collisions is a quite different mechanism of mass transport that occurs in the aquaporin. This makes molecules transport very fast within the pores of the cell membranes. Viceversa, the mechanism of mass transport of particles in the synthetic membrane pores is usually

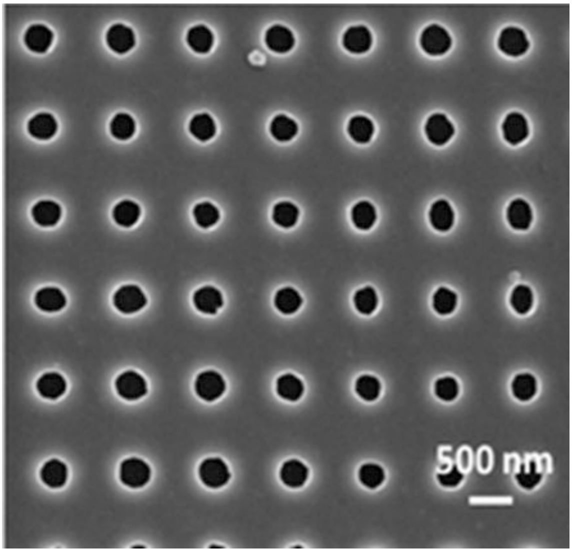


Fig. 3.1 Membrane structure formed by laser lithography. Reprinted with the permission from Ref. [30]. Copyright 2013 RSC

dependent on the ratio of the pore and the molecule size that are subject to the transport. The sharp pore distribution of membranes is always very welcomed and allows easier intensification of membrane processes through appropriate selection of a given process. However, in commonly applied membranes, there are differences in the sizes of pores and therefore the statistical approach is used to describe the pore size distribution. In practice, the free path of particles under given thermodynamic conditions is used instead of particle size:

$$\lambda = \frac{\eta}{P} \cdot \sqrt{\frac{\pi k T}{M}}. \tag{3.2}$$

The difference in electrochemical potential across the membrane $\Delta\mu$ (ΔC, ΔT, ΔP and ΔU) is generally the driving force of every membrane process (see in Fig. 3.2)

In the pressure-driven membrane processes, the flux through the membrane is proportional to the pressure difference across the membrane, i.e., transmembrane pressure ($\Delta P = P_{\mathrm{Ri}} - P_{\mathrm{Pi}}$), and inversely proportional to the thickness of the membrane l, where proportionality factor is membrane permeability K (see Eq. 3.3)

$$J_i = K \cdot \frac{P_{\mathrm{Ri}} - P_{\mathrm{Pi}}}{l}. \tag{3.3}$$

In the range of very small pores, i.e., lesser than 3 Å, which refers to a very large ratio of the $10 < \lambda/r < \infty$ it is considered that the membrane is nonporous (dense) such as the liquid layer and the transport mechanism is related mainly to the dissolution and diffusion (Fig. 3.3). Inside of the membrane, the transport of components is based on a simple diffusion due to Fick law (Eq. 3.4):

$$J_i = D_{iM} \frac{C_{\mathrm{Ri}} - C_{\mathrm{Pi}}}{l}. \tag{3.4}$$

However, before the diffusion through the membrane, the given component has to be dissolved in it first. The solubility of a component specifies the equilibrium between the membrane and the retentate side (Eq. 3.5):

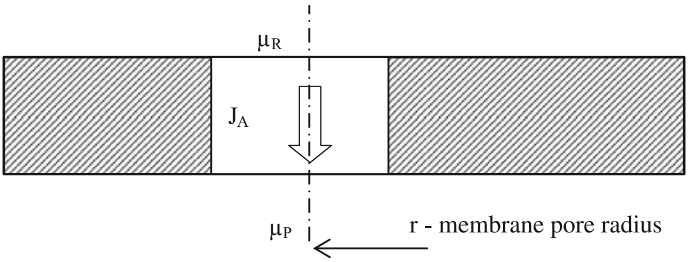


Fig. 3.2 The mechanism of mass transport of particles in the membrane pores

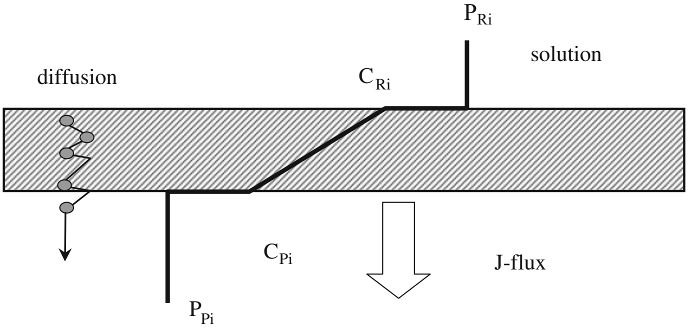


Fig. 3.3 The concentration profile of given component during solution-diffusion mechanism

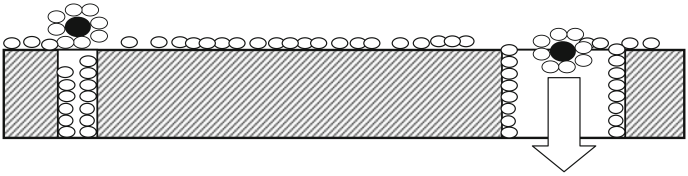


Fig. 3.4 Transport mechanism based on the finely porous model

$$S_i = \frac{C_{\mathrm{Ri}}}{P_{\mathrm{Ri}}}. \tag{3.5}$$

Therefore, the resultant permeability of the component depends on the product of solubility and diffusivity in the membrane (Eq. 3.6):

$$K_i = S_i \cdot D_{\mathrm{Mi}}. \tag{3.6}$$

It should be emphasized that the solubility can be much better controlled by appropriate selection of the membrane material than the diffusivity, which suggests it is the best way of intensifying the efficiency of separation in these membranes.

It should be added that the membrane separation for some processes can be controlled by selecting conditions of solution (concentration, ionic strength, pH, T) that allow for a change in hydration of membranes as well as separated particles. In this case, also the wettability of the membranes is important. The separation efficiency of these membranes may be determined by the heat (enthalpy) of particle hydration according to the finely porous model [14, 15]. In this regard, it is possible to further intensify membrane process in the very convenient way (Fig. 3.4).

For molecules within the range of 5–30 Å, which corresponds to ratio $1 < \lambda/r < 10$, the mechanism of mass transport is the Knudsen diffusion (Fig. 3.5).

In this case the appropriate diffusion coefficient must be determined taking into account also the membrane pore size:

$$D_K = \frac{2}{3} \cdot r \cdot \sqrt{\frac{8RT}{\pi M_i}}. \tag{3.7}$$

For pore size range of 30–30000 Å and a ratio $0.001 < \lambda/r < 1$, we are dealing with the transitional region. When the pore radius is above 30,000 Å and ratio $\lambda/r < 0.001$ transport mechanism is convective flow or the volumetric flow under the influence of a pressure gradient across the membrane (transmembrane pressure). This is the case for microfiltration and simple filtration. In the majority of cases, the membrane is only a passive barrier to the permeate flow and there is not chemical interaction between the flowing particles and the membrane. However, there are also membranes where the mass transport of selected components is coupled to a chemical reaction, thereby enhancing the selectivity of separation (Fig. 3.6).

3.3 Intensification of Processes Through Appropriate Design and the Choice of Membrane Modules

The main criteria for the selection of membranes in terms of intensification of membrane processes were discussed in the last section. This section is devoted to the selection of appropriate conditions on the surface of the membrane. The so-called "concentration polarization" is the phenomenon of the occurrence of concentration boundary layer at the membrane surface. This is an inherent phenomenon accompanying each membrane separation (Fig. 3.7).

The membrane resistance R_M exerts the major effect on the flux when either solution flows freely through the membrane.

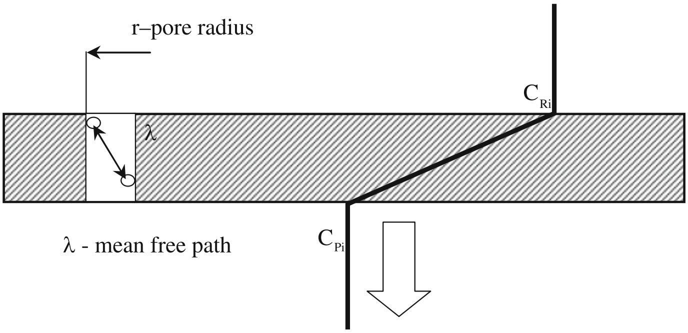


Fig. 3.5 The Knudsen diffusion mechanism

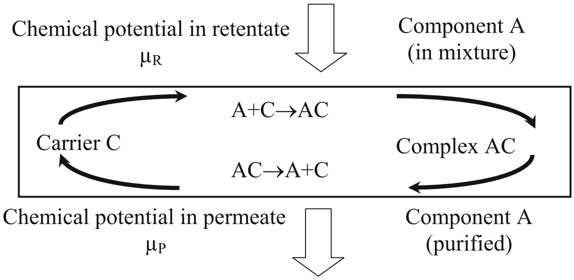


Fig. 3.6 Mechanisms of facilitated transport (for $\mu_R > \mu_P$) and active transport (for $\mu_R < \mu_P$)

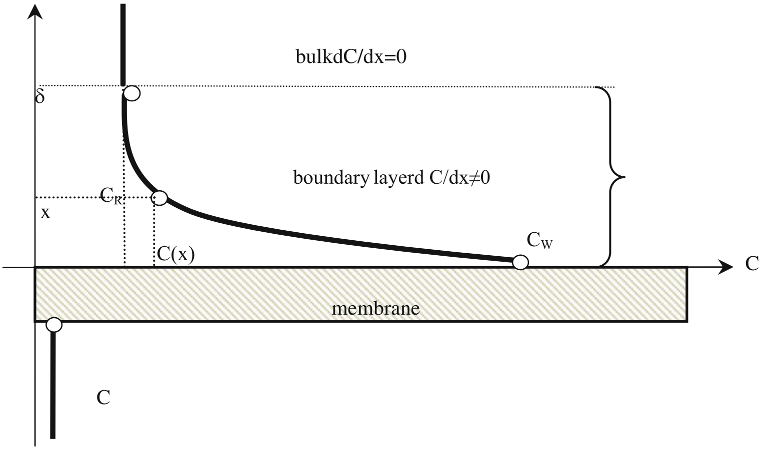


Fig. 3.7 Concentration polarization

$$\text{if retention} \quad R = \frac{C_R - C_P}{C_R} = 0 \quad \text{then} \quad J = \frac{\Delta P}{R_M}. \tag{3.8}$$

However, in the real membrane separation, the substances retained at the membrane surface also affect the permeate flux. The additional resistance R_w depends on the concentration (C) of the substance at the membrane surface.

$$\text{if retention} \quad R = \frac{C_R - C_P}{C_R} > 0 \quad \text{then} \quad J = \frac{\Delta P}{R_M + R_W(C)}. \tag{3.9}$$

Apart from the resistance of the layer (R_W), the additional effect of reducing the driving force is an osmotic pressure ($\Delta\pi$). This occurs in the cases of higher concentrations of solutes with lower molecular weight. In this way, the transmembrane pressure (ΔP), as a main driving force of membrane process, is reduced, as well as the permeate flux (J) (see Eq. 3.10 below):

$$J = \frac{\Delta P - \Delta\pi(C)}{R_M + R_W}. \tag{3.10}$$

It should be noted that the effect of concentration polarization is evident in many different processes. The graphs below have identified the phenomenon of concentration polarization for three pressure processes such as RO, UF, and MF (Fig. 3.8). The effects of concentration polarization are called and interpreted in different ways as limiting flux, flux paradox, and critical flux.

In the widely used "film model" a simple approach is used, by limiting only to the steady-state process. According to the film model, the convective inflow of the substance to the membrane is counterbalanced by the diffusive outflow from the boundary layer in opposite direction (Fig. 3.9). It is assumed that the accumulation is zero and the boundary layer thickness is constant. So the film model can describe only stationary processes.

Balance of the retained mass at the membrane surface leads to an ordinary differential equation of the form (Eq. 3.12):

$$J \cdot C(x) = -D \cdot \left|\frac{\mathrm{d}C}{\mathrm{d}x}\right|_{x=0} + J \cdot C_P \tag{3.12}$$

After taking into account a boundary condition (C (0) = C_W), the basic equation is obtained to calculate the permeate flux for a membrane with limited retention:

$$J = k \cdot \ln\left|\frac{C_W - C_P}{C_B - C_P}\right| \quad \text{where} \quad k = \frac{D}{\delta}. \tag{3.13}$$

The rate of mass transport depends on the film thickness of the border depending on the turbulence. Therefore, the thickness δ of the boundary layer (film) is the kinetic parameter for a "film model" that can be controlled by proper selection of

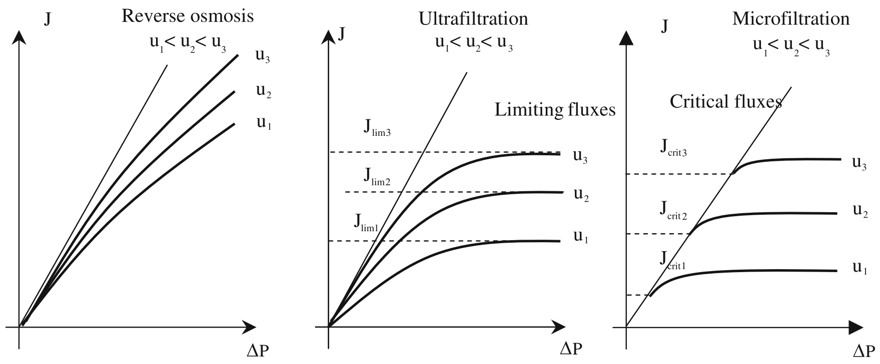


Fig. 3.8 Effects of concentration polarization on flux in RO, UF, and MF. Reprinted with the permission from Ref. [17]. Copyright 2014 De Gruyter

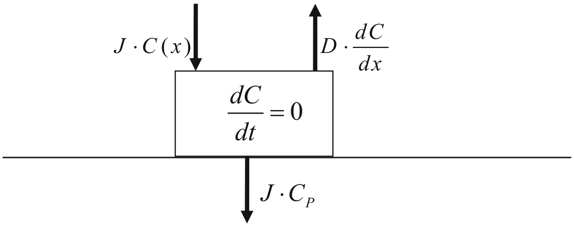


Fig. 3.9 The assumptions of the film model at steady-state conditions

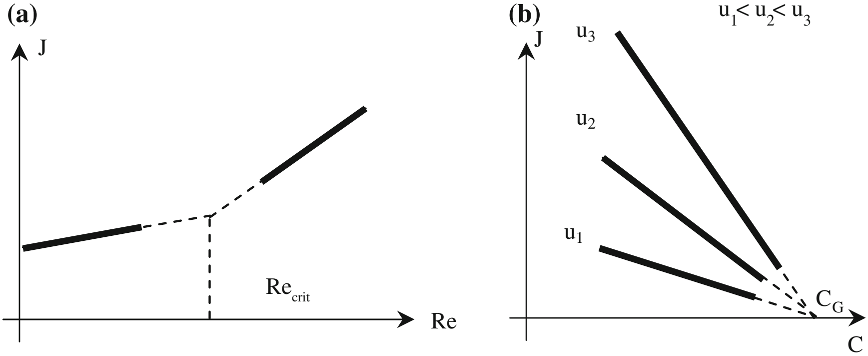


Fig. 3.10 The influence of velocity (**a**), and concentration (**b**) on permeate flux

the cross-flow velocity and the type of module. Concentration at the wall is constant $C_W = C_G$ and is called as gel concentration. In the case of ($R = 1$ and $C_P = 0$) a simpler formula (Eq. 3.14) on the permeate flux may be used:

$$J = k \cdot \ln\left|\frac{C_G}{C_B}\right|. \tag{3.14}$$

It can be seen that when the flow rate increases the flux increases too, but also evident is the discontinuous effect of varying the flow regime (Fig. 3.10a, i.e., effect of turbulence). The graph (Fig. 3.10b) shows that the flow decreases with the increase of retentate concentration, and the lines converge at the same point called the gel concentration (C_G).

Microfiltration as the sole membrane process is a kind of mechanical filtration of particles in the micron range. Despite the similarities with ultrafiltration (see Fig. 3.8), wherein the line describing the flow is also leveling off on constant level depending on velocity which is tangential to the membrane surface though the phenomenon of concentration polarization is quite different. The phenomenon of so-called critical flow can occur when the separated particles are the same size. Critical flux can be used during the “cold sterilization” bringing many benefits. Initially, at low pressure and thus low flux (below the critical flux), the permeate

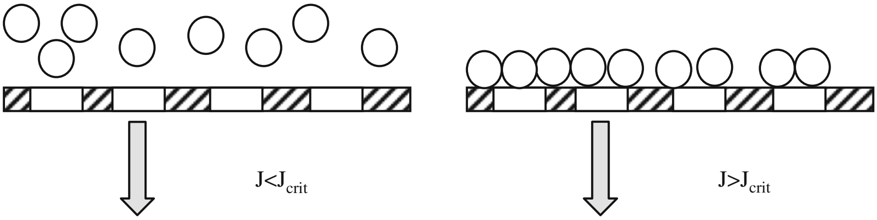


Fig. 3.11 The critical flux phenomenon

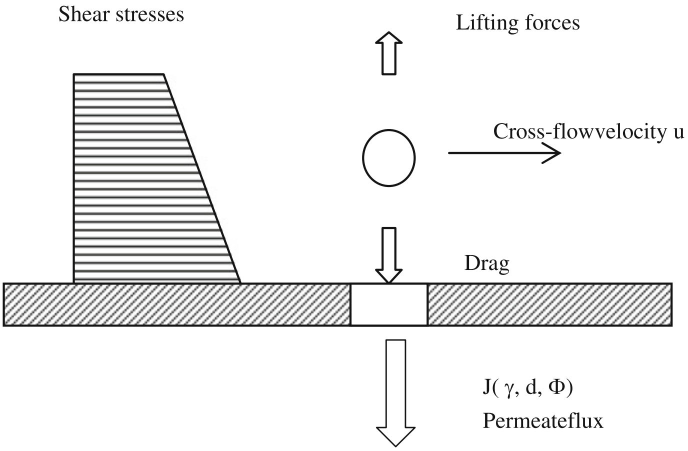


Fig. 3.12 The principal of critical flux MF. Reprinted with the permission from Ref. [17]. Copyright 2014 De Gruyter

stream is equal to flux of pure solvent because the particles do not come into contact with the surface of the membrane (Fig. 3.11).

This phenomenon results from the balance between the drag forces that push particles into the pores together with the permeate flux, and the lifting forces in the direction opposite to the membrane (Fig. 3.12). It is still not known, which are the real reasons for this phenomenon. It is clear that the main cause is the shear stress at the surface of the membrane influenced by the rheological properties of the fluid.

The permeate stream is the most important parameter used to intensify all the membrane processes. The common way to ensure a high flux is the use of the cross-current flow of permeate stream relative to the retentate (see Fig. 3.13) in order to reduce the concentration polarization layer. However, the cross-flow requires large amounts of energy to achieve the correct speed. For this purpose, the most common circulating ratio is even to 100. Therefore, in addition to the cross-flow, a large number of other methods for increasing the permeate stream are used. The recirculation of retentate allows the creation of optimal hydrodynamic conditions in the modules of various constructions. In the modules with the larger flow channels (with hydraulic diameter of above 2 mm) it is possible creation of the turbulent flow, which is dominated by eddies. In the modules with the smaller size of the flow channels such as hollow fiber, spiral wound, or flat panels, the effects of shear forces lead to a reduction of concentration polarization effect. Also the meshes for specific flow configuration are used at spiral wound modules. Also other methods are used to reduce the boundary layer of concentration such as the use of abrasives, foam beads, betonies, diatomaceous earth, and injection of gas into the retentate stream and rotation of membranes. The pulsations at different scales periodically change the direction of permeate flow; ultrasounds and electric field are also used. All of these methods can be applied only in a specific and very narrow range of applications. One of the most versatile methods is to use back pulsing, which is a periodic and very short reverse of the permeate flow which sometimes can unlock the pores in the membranes and causes a temporary increase in the permeate flux [9].

It is very important for the intensification of membrane process to choose the appropriate module with the cross-flow. The membrane module is a repeatable device where the cross-current flow of retentate and permeate streams is applied. The following types of modules are widespread in the market [9]:

- Tubular
- Capillary (hollow fiber)
- Spiral wound
- Flat plate (plate and frame)
- Immersed membrane module.

Proper selection of the membrane module in the given process is also a part of the intensification of the process and the designers should always do so in a thoughtful way because they have many possible variants. Each of the module types has specific properties that are appreciated by users. Tubular modules have a very simple construction, a high mechanical strength, and are used commonly in the

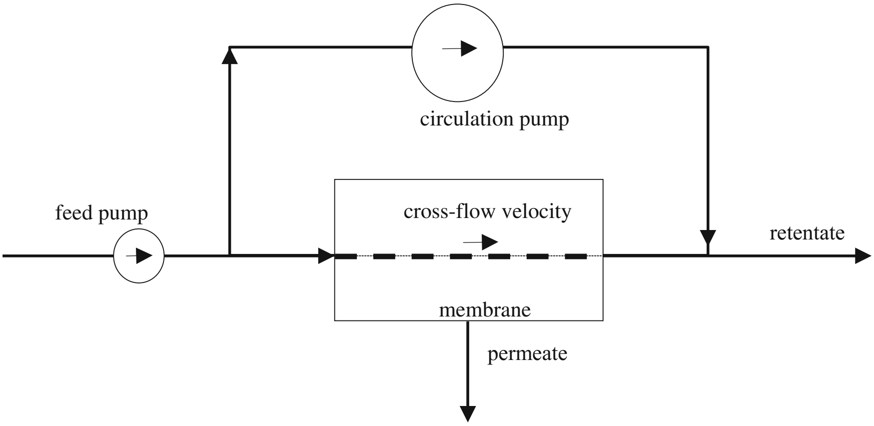


Fig. 3.13 Cross-flow principle

contaminated fluids. The modules with hollow fibers (d < 0.5 mm) reveal a large membrane surface in a small volume, and can withstand very high pressures. The capillary modules (0.5 mm < d < 2 mm) are a compromise between the pipe and hollow fiber. The flat modules (or plate and frame) are recommended in the case of the extremely high pressures. They are used in cases where a high degree of concentration is required and the increased viscosity of the retentate makes greater resistance to flow. Spiral modules also withstand high pressure, and are readily used due to low cost, large specific area, and the possibility to easy exchange in case of failure.

A very economical way to obtain a high permeate flux without the high cost of energy consumption is the use of so-called submerged membrane modules [24] (Fig. 3.14) or reactors [25]. In such cases, very small streams but the large surfaces of the membranes are used. The membranes are freely immersed in the tank with the feed stream, wherein the permeate stream is collected inside the capillary or permeate side of flat membranes, and then collected in a suitable manifold. The permeate stream flows out under a small hydrostatic pressure or under the small vacuum, and the filter cake does not adhere strongly to the surface of the membrane. In this case, the cake can be removed from the membrane surface due to spontaneous and small waving movements of the membranes.

Another technical problem which occurs in membrane systems is time. In fact it is well known that this is a far-fetched assumption and membranes are not operating at stable conditions due to the continual decrease in permeate stream ("flux decline") under the influence of concentration polarization and fouling (See Fig. 3.15). It is difficult to maintain the installations in the strictly stationary operation, even when operating conditions are unchanged.

In order to maintain high intensity of membrane processes, the permeate flux is maintained at the possible maximum level through periodic cleaning of the membranes. But this popular method also has many disadvantages. First, it is necessary to stop the process for cleaning. Second, the resulting wastewater needs to be

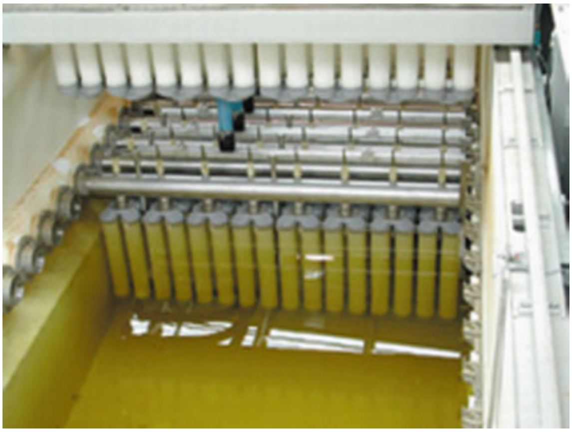


Fig. 3.14 Submerged hollow fiber modules of MEMCOR. The world's largest CMF-S pure water treatment facility with the capacity of 126,000 m^3/day is in operation in Bendigo, Victoria, AustraliaMF. Reprinted with the permission from Ref. [28]

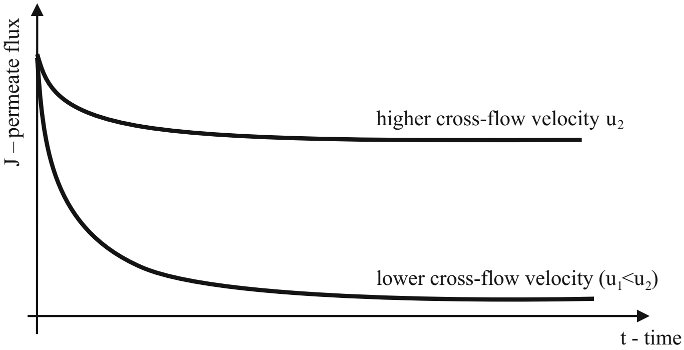


Fig. 3.15 Flux decline

Fig. 3.16 Cleaning in place plantMF. Reprinted with the permission from Ref. [29]

disposed skillfully and the recovery of cleaning substances is difficult and the recovery of the product bleed is rather problematic. Third, using the cleaning agents increases the cost. Therefore, the skillful handling of washing procedures and their time requires the introduction of optimization and automation of procedures (Fig. 3.16). For economic reasons, such strategies are used primarily for large installations (more than 100 m^2) surface membranes.

During operation with the multiple cycles, there is a change in the flux between subsequent cycles of regeneration (Fig. 3.17), which is called flux decline. Thus flux decline exerts the effect on the average flux during the operation:

$$\bar{J}_{av} = \frac{1}{n}\sum_{i=1}^{n}\frac{1}{t_{pi}+t_{ci}}\int_{0}^{t_{pi}} J(t_{pi})\mathrm{d}t_{pi}. \tag{3.15}$$

A very effective way to intensify cyclic process is optimal selection of process time and cleaning time (Fig. 3.17). When integrated formula 3.15, we get the average value of permeate flux during cyclic operation, taking into account the time

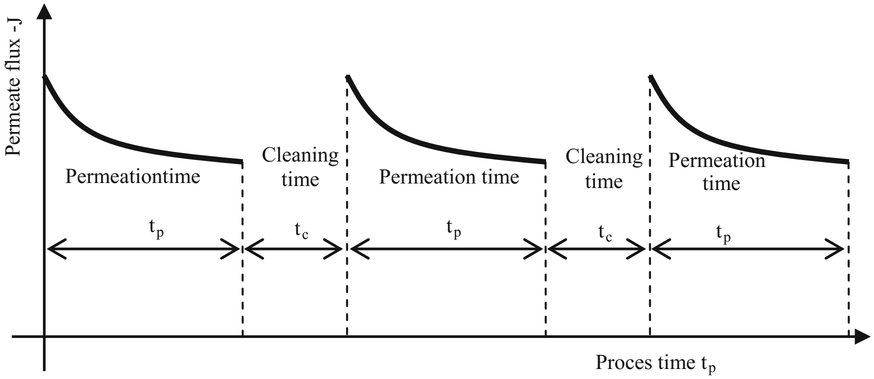


Fig. 3.17 Cyclic mode of membrane process operation [16], where t_p—process (permeation) time and t_c—cleaning time

of cleaning and permeation. Such an optimization procedure requires an accurate description of the flux decline during the process. Unfortunately, it is always very tedious and difficult to predict the flux decline based on the film model. With respect to the membrane processes, it seems to be much easier to use the modified surface renewal model, as shown in several publications by Koltuniewicz [16, 17, 19, 20, 22, 23]. Initially, the surface renewal model has been proposed by Danckwerts [18], for the absorption, but it is also applicable for any other unit processes provided that it is operated under stationary conditions. Such a relationship has been proposed in the literature as the equation (Eq. 3.16), which describes the change in the permeate flux (flux decline) by the modified Danckwerts model:

$$\bar{J}(t_p) = (J_0 - J^*)\frac{s}{A+s}\frac{1 - \mathrm{e}^{-(A+s)t_p}}{1 - \mathrm{e}^{-st_p}} + J^*. \tag{3.16}$$

An intensification of any membrane process requires a quite different approach, when the flux depends mainly on the membrane properties or when the concentration polarization layer is dominant. In the first case it is evident that the flux can be adjusted only by choosing the appropriate membrane, and in the second case various ways to reduce concentration polarization at membrane vicinity should be applied on. The Hermia model could be recommended to this end.

Hermia's model [21] describes all filtration cases by means of one formula (Eq. 3.17):

$$\frac{\mathrm{d}^2 t}{\mathrm{d}V^2} = k\left(\frac{\mathrm{d}t}{\mathrm{d}V}\right)^n. \tag{3.17}$$

In this formula the V is the filtrate volume and the t is the filtration time. Parameters "k" and "n" must be determined empirically based on the identification procedure. Considering the nature of the filtrate volume changing over time, the four types of filtration can be distinguished based on the value of the n parameter. When the filtration is dominated by complete pore blocking in the membrane $n = 2$, then it is best to change the type of membrane for the smaller cut-off. In the cases when filtration is dominated by the layer at the membrane vicinity (cake or polarization) then $n = 0$. Besides, in Hermia model are listed two other cases of so-called standard pore blocking ($n = 3/2$) and transient pore blocking ($n = 1$). Thus, the identifying the n parameter values allows for the accurate localization of the main resistance based on experimental observations of the flux decline. Then the best actions for the intensification of the membrane process may be undertaken.

According to cake mechanism in the Hermias model (n = 0), the elements separated are collected only at the membrane surface forming a layer ("cake") which causes an additional resistance for permeate flow. The resistance coefficient can be expressed by the following formula:

$$k = \frac{\alpha \cdot \rho_s \cdot \phi}{A^2 \cdot R_0 \cdot J_0 \cdot (1 - m \cdot \phi)}. \tag{3.18}$$

At any moment the total resistance is the sum of the membrane resistance (R_0) and cake resistance. The cake height increases proportionally to volume (V) of the permeate flux. Specific cake resistance (α) is constant, and m is the ratio of dry mass of the cake to the wet mass, A—cross-sectional area of pores and Q_0—volumetric flow rate.

In the opposite case, i.e., completely pore blocking the value of $n = 2$, the membrane is responsible for the flux. In this case, the coefficient of resistance may be expressed as follows:

$$k = 1.5 \cdot \frac{\rho_\mathrm{S} \cdot \phi}{\rho_0 \cdot d \cdot \psi} \cdot J_0, \tag{3.19}$$

where ρ—density, subscript 0 refers to suspension, subscript s refers to solid particles in suspension, ϕ—mass ratio of dispersed material, d—apparent diameter, ψ—shape coefficient, J_0—filtrate flux, and A—cross-sectional area of pores.

Unfortunately, determination of both parameters (m and k) directly from the model Hermia is very inaccurate. This happens because of the necessity for calculation of derivatives (especially second order) on the basis of the experiment resulting in large errors even at very carefully performed measurements of volume in time $V(t)$. The modification in the model Hermia has been proposed in the literature [22, 23], in which the model parameters can be determined directly by measuring the flux decline (Eq. 3.20):

$$J(t) = \left[J_0^{(n-2)} - R \cdot A^{(2-n)}(n-2) \cdot t\right]^{\frac{1}{(n-2)}}. \tag{3.20}$$

The use of this modified Hermias formula is free from the risk of error when we use experimental measurements of the flux decline in real time instead of the derivatives. It should be noted, however, that the possibility of even all the mechanisms may be present consecutively during the experiment. This happens as a result of the fuzzy pore size distribution in bad-quality membranes. However, the selection of the good quality membrane with a narrow pore distribution mechanism should allow appropriate selection of cut-off point of the membrane. Then all the particles should be retained only on the surface of the membrane exclusively (cake mechanism $n = 0$), and can then be removed from it by cross-current flow mechanisms.

3.4 Intensification of Membrane Processes Through System Configurations

One of the ways of intensifying the membrane may be the right choice of configurations across the membrane plant and its proper design [19]. In larger plants, the configuration of the system is very important. To enhance the plant efficiency the modules can be interlinked in a specific way depending on the goals.

The main product of membrane systems may be retentate (e.g., concentrating) or permeate (e.g., purification). If the primary goal of membrane separation is to purify, the maximum degree of purity and maximum recovery of the permeate (RC) must be predicted:

$$\mathrm{RC} = \frac{m_P}{m_F}. \tag{3.21}$$

If the main task of membrane separation is the concentration of the given component the maximum profitable degree of concentration should be assumed. Concentration factor is defined as follows:

$$\mathrm{CF} = \frac{C_R}{C_F}. \tag{3.22}$$

Besides, it should be determined what is in addition to the main component, whether to recover or whether somehow pretreatment should be arranged? It also needs to be considered whether the required separation membrane stage can be carried out in the simplest way, or whether some additional method must be used such as the recycling, by-passes, or more number degrees of separation. Based on the mass balance on given membranes the appropriate formulas for calculating concentration in the permeates (Eq. 3.24) and the retentates (Eq. 3.23) streams for single separation stage (Fig. 3.18) could then be determined:

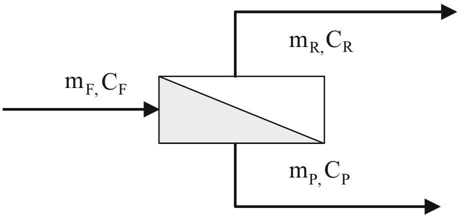


Fig. 3.18 The single separation stage

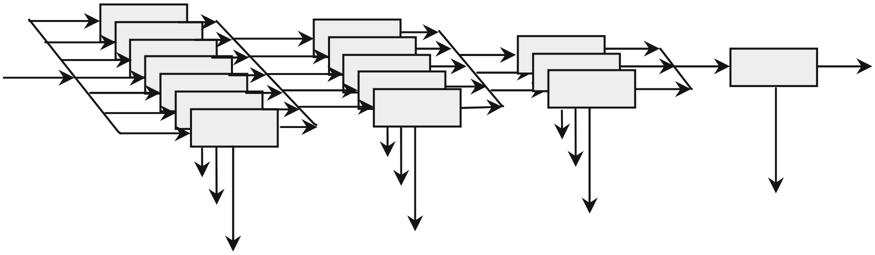


Fig. 3.19 The multistage separation system "Christmas tree"

$$C_R = C_F \cdot \frac{1 - \mathrm{RC} \cdot (1 - R)}{1 - \mathrm{RC}} \tag{3.23}$$

$$C_P = C_F \cdot (1 - R). \tag{3.24}$$

Usually in the multistage systems, the flow rates of the retentates are reduced adequately since permeate outflows. This can be compensated by reducing the number of modules in subsequent sections, known as a "Christmas tree" (see Fig. 3.19).

A good way to increase the "concentration factor" is to use recirculation of the retentate (Fig. 3.20)

If the (n) means ratio of the flow rates of the circulation (m_C) and retentate (m_R), the retentate concentration for this system can be calculated from the mass balance as

$$C_R = C_F \cdot \frac{(1 - n \cdot (1 - \mathrm{RC})) \cdot (1 - \mathrm{RC} \cdot (1 - R))}{(n \cdot (\mathrm{RC} \cdot (1 - R) - 1) + 1) \cdot (1 - \mathrm{RC})}. \tag{3.25}$$

And so we calculate the concentrations in the permeate stream for such a system:

$$C_P = C_F \cdot \frac{(1 - R) \cdot (1 - n \cdot (1 - \mathrm{RC}))}{n \cdot (\mathrm{RC} \cdot (1 - R) - 1) + 1}. \tag{3.26}$$

The single-stage membrane systems with bypass can be used to obtain the largest permeate recovery as possible (Figure 3.21).

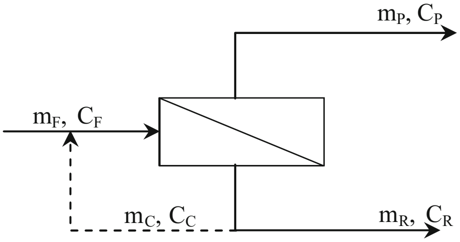


Fig. 3.20 The single-stage membrane system with recirculation $n = m_C/m_R$

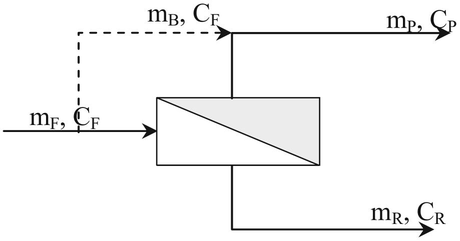


Fig. 3.21 The single-stage membrane system with bypass $j = m_B/m_F$

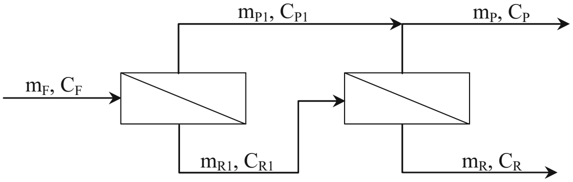


Fig. 3.22 The two- stage membrane system, with collecting of the permeate

In such a system, the permeate stream can be increased and the concentration in the permeate stream can be adjusted (upward only) to the standards or other requirements:

$$C'_P = C_F \frac{\mathrm{RC} \cdot (1 - j) \cdot (1 - R) + j}{\mathrm{RC}(1 - j) + j}. \tag{3.27}$$

The concentration in the retentate stream can also be determined based on the mass balance:

$$C_R = C_F \cdot \frac{1 - \mathrm{RC} \cdot (1 - j) \cdot (1 - R) - j}{1 - \mathrm{RC} \cdot (1 - j) - j}. \tag{3.28}$$

In order to further improve the separation parameters, the so-called cascade membrane systems can also be used. Depending on the connection method the two basic types of the systems can be distinguished, i.e., multistage or multipass systems. The multistage systems are those where permeate streams from subsequent membrane modules are collected in parallel, wherein the retentate streams are combined in series. In multi-pass systems the retentate streams are collected in parallel, whereas the permeate streams are connected in series. Example of two-stage membrane cascade is shown in Fig. 3.22.

To calculate the concentration in the retentate and permeate streams, we can use the following formula derived from the mass balance (i.e., the laws of conservation of mass):

$$C_R = C_{R2} = C_F \cdot \left[\frac{1 - \mathrm{RC} \cdot (1 - R)}{1 - \mathrm{RC}}\right]^2 \tag{3.29}$$

$$C_P = C_F \cdot \frac{2 - \mathrm{RC} \cdot (1 - R)}{2 - \mathrm{RC}} \cdot (1 - R). \tag{3.30}$$

When the retentate streams are connected together and permeate streams are passing through successive stages of purification, then we call this system as a multi-pass systems (Fig. 3.23). This configuration is preferred when the main product is the permeate.

In this case, the appropriate concentrations of the retentate and the permeate streams may be calculated from the following formulas.

$$C_R = C_F \cdot \frac{1 - \mathrm{RC}^2 \cdot (1 - R)^2}{1 - \mathrm{RC}^2} \tag{3.31}$$

$$C_P = C_F \cdot (1 - R)^2. \tag{3.32}$$

The multi-pass membrane system, with recirculation of the retentate (Fig. 3.24), seems to be the best solution of the plant, with respect to the yield and selectivity of separation.

In this case the corresponding concentrations in the retentate and the permeate streams can be calculated as follows:

$$C_R = C_F \cdot \frac{[1 - \mathrm{RC} \cdot (1 - \mathrm{RC})] \cdot [1 - \mathrm{RC} \cdot (1 - R)]}{[1 - \mathrm{RC} \cdot (1 - R) \cdot (1 - \mathrm{RC} \cdot (1 - R))] \cdot (1 - \mathrm{RC})} \tag{3.33}$$

$$C_P = C_F \cdot \frac{[1 - \mathrm{RC} \cdot (1 - \mathrm{RC})] \cdot (1 - R)^2}{1 - \mathrm{RC} \cdot (1 - R) \cdot (1 - \mathrm{RC} \cdot (1 - R))}. \tag{3.34}$$

Fig. 3.23 The two-pass membrane system, with collecting of the retentate

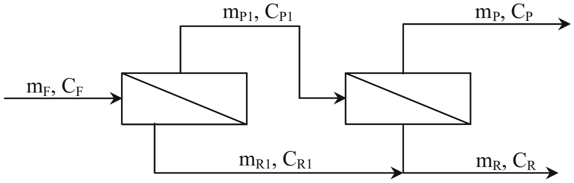
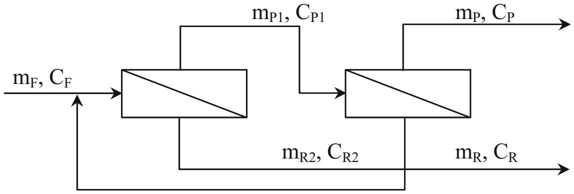


Fig. 3.24 The two-pass membrane system, with recirculation of the retentate



The comparison of the above-mentioned configurations reveals the big potential for intensifying any given process by the appropriate design, where the productivity and separation may be increased while the total costs are being reduced. Generally, the two last configurations, e.g., two-pass systems, give the maximum selectivity of separation, whereas the system with recirculation offers the better concentration factor. When the main product is the retentate which has to be concentrated in maximum extent, the multistage systems are recommended because they offer the maximum retentate concentration. The two-pass systems are recommended when splitting factor SF should be intensified, for example, in separation of toxic or valuable substances. However, the single-stage configurations are obviously much cheaper.

3.5 Membrane-Based Hybrid Processes

In order to increase the efficiency of the separation, the membrane process can be integrated with other "unit separation processes" [26]. The combinations of processes that are similar in function but different in terms of physical are called hybrid processes. The hybrids allow for better optimization of parameters, because the number of degrees of freedom is greater. Some authors distinguished two main types of hybrid processes. The first of these relates to the combination of separation processes, whereas the second group of hybrids is the combination of the separation with the chemical reaction. It should be noted that hybrids are often formed by a simple structural connection of devices (lower degree of integration) or the integration of the same functions in one unit (higher degree of integration).

A typical example is the combination of the hybrids with a lower degree of integration, as pervaporation membrane modules with distillation columns. The unit processes that make up the hybrids are based on different physical mechanisms leading to the final separation target. This combination ensures the functioning of the same separation role, which may be, for example, the separation of the solvent from the water or vice versa. The main distinguishing feature of the separation of components is their solubility in the pervaporation membrane, and in the case of the distillation are differences between volatilities of the components. In addition to large savings in energy and financial resources hybrid processes allow to solve additional problems as the presence of azeotropes in this case. The number of hybrid processes that are possible to design is very large considering the great number of subprocesses. During wastewater treatment, it is worth considering the possibilities of easy recovery of individual components using a hybrid process. For example, combination of pervaporation with nanofiltration enables the recovery of valuable organic and inorganic substances. The use of electrodialysis with reverse osmosis, nanofiltration, or ion exchange allows for easy separation of ionic substances from nonionic. In addition, it is a possible separation of specific fractions, thanks to the new membranes with a narrow size range of particles separated (cut-off). It should be added that the ability to easily recover substances from sewage and other multicomponent mixtures is the indispensable prerequisite for the design of clean technologies, which today set the direction for the development of modern industry. So-called by-products may be used by other sectors whereas the reduction of waste is an additional effect in the direction of sustainable development. In the hybrid designing for wastewater treatment, several types of specific reactors are used, such as bioreactors, photoreactors, and photo-bioreactors for bio-oxidation, photo-oxidation, and denitrification (Fig. 3.25).

The rapid development of hybrid processes results in a number of inconsistencies as to their classification. Such devices, for example, catalytic membranes, affinity membranes, or membrane contactors, are in fact also hybrid, by integrating several functions in one device instead of integrating the devices themselves.

The processes accomplished in these contactors are membrane distillation, membrane extraction, membrane absorption, or membrane adsorption. In this case, the different unit processes are integrated with the membrane separation. It is not just for reducing the dimensions of these devices, but additional effects of process intensification may be also achieved. For example, in the membrane distillation the considerable energy savings are achieved because the evaporation takes place without boiling at a minimum temperature difference between the feed and the

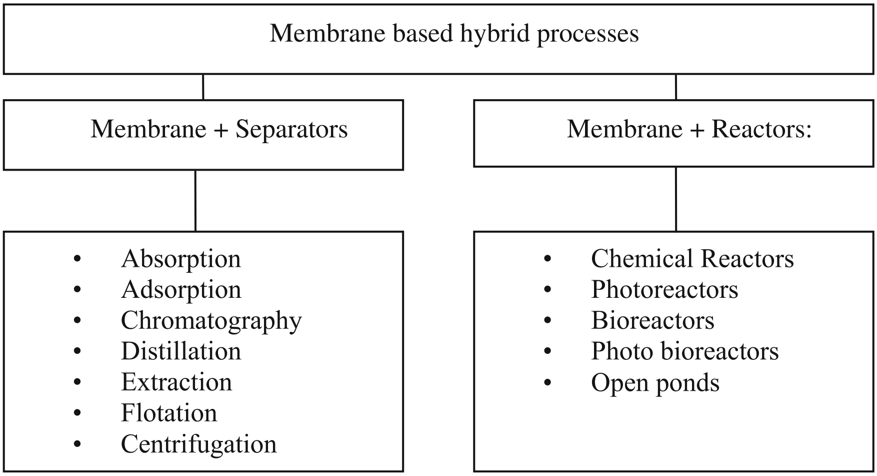


Fig. 3.25 Hybrids with lower degree of integration

distillate, thereby making it possible to utilize the so-called waste heat. Another example of an additional benefit is the use of membrane contactors to the so-called membrane extraction. It is even possible to use the membrane extraction for two aquatic solutions when using the hydrophobic membranes on one side and on the other sides having the hydrophilic properties. This eliminates a number of hazardous solvents in the manufacture of medicines, food, and feed. The membrane absorption permits water solubility of gaseous components in liquids while minimizing the losses which occur during the conventional barbotage in columns and the reactors. It is very important in different reactors, during the cultivation of algae at photo-bioreactors, and the carbonation of different beverages (Fig. 3.26).

A very important hybrid of a high degree of integration which is suitable for process intensification is to combine a function of separation with the chemical reaction at the reactive membranes. This is not a simple combination of the reactor with the membrane, but immobilization in the membrane pores or on its surface of a variety of chemically active elements. These elements can be, for instance, catalyzers, enzymes, functional groups, electrical charges, cells, and tissues. In the case of affinity membranes the ligands used are amino acids; antigen and antibody ligands; dye ligands; metal affinity ligands, chelate adsorbents, ion exchange ligands, peptides, and thiophilic adsorbents. As the catalysts are usually used following metals: Cu, Co, Ni, Cr, Fe, Pt, Pd, Ru, Mo, Pc, and Y. The catalytic membrane enables efficient contact between the three phases which allows to adjust the rate of reaction. Catalytic membranes can provide as much as 50% higher yields than conventional reactors. Catalytic membranes are used in chemical industry for

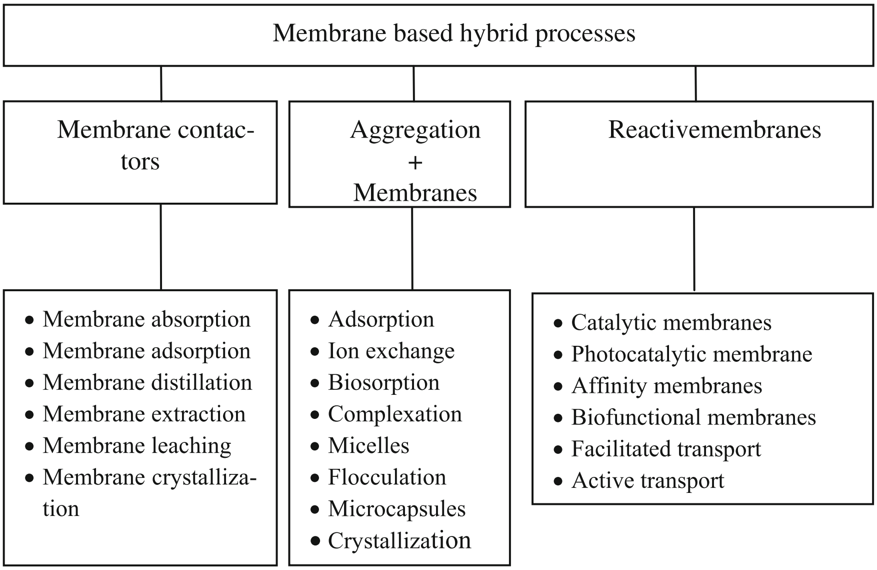


Fig. 3.26 Hybrids with higher degree of integration

the various types of reactions such as oxidation, hydrogenation/dehydrogenation, oligomerization, dimerization, epoxidation, and reforming. A very good example is the intensification of the membrane chromatography process. In this case the every single pore in the membrane serves as a whole chromatography column. The flow through the several meters of adsorbent layer, in affixing the appropriate ligands, is adapted for the industrial chromatography columns. The efficiency of separation in the column chromatography depends on the column height, because the collision probability of separated molecules and the ligand is the greater, the longer is their residence time in the column. In the membrane chromatography, the same probability is increased by appropriate selection of the pores of the membrane. Needless to say, the thickness of the membrane is much smaller (on average 100 μm) than several meters height column. Membrane chromatography is a very interesting example of intensification as a hybrid process. The intensification is, in fact, obtained by reducing the energy consumption and the size of the apparatus at the same time.

Another important hybrid technology is the electrochemically driven membranes, such as solid polyelectrolytes (SPE), which combine the function of reaction and separation. The modern applications of the SPE are production of hydrogen and oxygen from water, production of ozone, separation of isotopes: deuterium hydrogen, hydrogen absorption, water treatment, elimination of nitrates, electronically induced gas separation, sensors and fuel cells [27]. In pharmaceutical industry membrane-based hybrid processes are used for production of most important pharmaceuticals such as antibiotic, vaccines, peptides, and enzymes. Moreover, they are used for fractionation of proteins mainly plasma, for purification of enzymes, hepatocyte growth factor (HGF), and the monoclonal antibodies.

Membranes and membrane-based hybrid processes are used for removal of viruses, removal of endocrine disruptors, and removal of estrogenic hormones and endotoxins. They are used also for extremely difficult separation of enantiomers showing high efficiency and intensification of these processes in every respect.

3.6 Concluding Remarks

It seems that intensification of membrane processes must take into account broad multidisciplinary areas because of the complexity of the problem. They relate to process engineering, transport phenomena, chemistry, physics, and especially nanotechnology and materials science. The intensification is dependent on the membrane itself, as well as the phenomena occurring during its operation. It is important to make first the accurate selection of the membranes with respect to their structure properties, as the chemical compatibility and working conditions during operation and during cleaning. Due to the sensitivity of the membranes on various factors, the environment in which they work must accurately be identified. The engineering aspects of intensification of membrane processes will appear after making the correct selection of membranes that should include all aspects of handling and operation of the membranes. Then the selection of a type of membrane module, installation configuration, and selection of appropriate operating parameters should be implemented. At this stage, it is necessary to take into account economic factors related to the intensity and long-term durability of work, investment costs as well as expenditure costs for energy, maintenance, and materials. The surface area of the membranes is of crucial importance for all cost components in membrane installations and therefore the biggest possible fluxes are required. On the other hand, it is obvious that high permeate fluxes lead to excessive energy consumption and require additional investment and the appropriate procedures to prevent the concentration polarization as well as the membrane fouling. It is also possible premature destruction of the membranes and the installation. All these factors are interrelated and, therefore, proper design and operation of membrane plants require knowledge and engineering practice.

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Chapter 4
Sustainable Route in Preparation of Polymeric Membranes

A. Figoli, T. Marino, F. Galiano, S.S. Dorraji, E. Di Nicolò and T. He

Abstract Polymeric membranes are the most used separation media at industrial level, in biomedical, food, and water treatment fields, thanks to the easy preparation techniques, high flexibility, and low cost. Membrane separation has been recognized as a green sustainable process, the preparation route of polymeric membranes is still based on the use of toxic solvents and fossil-based polymers, which is not yet green and sustainable. Recently, an increasing number of research studies were reported, which referred to the possibility of producing polymeric membranes by using less-toxic solvents and biomaterials. This chapter is an overview of the polymeric membranes applied in desalination, water, and wastewater treatment, including biomaterials and the use of nontoxic solvents in membrane preparation. Finally, a cost analysis of polymeric membrane production comparing toxic and nontoxic solvents and the possibility of solvent recovery is also discussed.

Keywords Polymeric membranes · Polymeric membrane preparation · Green solvents · Bio-material · Polymeric membranes in water treatment · Membrane processes · Cost analysis in membrane preparation · Polymeric hollow fiber membranes

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4.1 Introduction

Increasing demand for and shortage of clean water as a result of rapid urbanization, population growth, misuse, and climate disruption have become unprecedented urgent global issues [1]. The World Water Council estimates that by 2030, 3.9 billion people will live in "water scarce" regions [2]. Therefore, cost-effective technologies must be developed to extend water resources and solve water pollution problems. Membrane water treatment is simple in concept and operation, does not involve phase changes or chemical additives, and can be made modular for easy scale up; and it is expected to perform an increasingly important role in the fields such as drinking water treatment, brackish, and seawater desalination, and wastewater treatment and reuse [3, 4]. Compared with the other types of membranes, polymeric membranes lead the membrane separation industries and markets due to their straight forward pore forming mechanism, higher flexibility, smaller footprints required for installation, and relatively low costs compared to inorganic membranes equivalents [3, 5–7].

To fully respond to the requirements related to the reduction of waste generation, thus for the conservation of living species, membrane technology should require the support of nontoxic substances, in accordance with the basic principles of green chemistry [8], as shown in Fig. 4.1.

Although the preparation of polymeric membranes obtained from biological matrices is still at the very early stage of development, recently it has been highlighted that the scientific research is in the right direction and gradually replace conventional petroleum-based materials with more sustainable alternatives is highly probable [9]. The choice of the solvents used in the membrane preparation process play an equally important role for achieving a completely green membrane process. In fact, largely employed diluents comprise serious hazards compounds, which impede the possibility to preserve the natural, clean environment, and to improve the quality of human life. Their substitution with more sustainable, preferably bio-based, solvents represents one of the major challenges for the membrane technology [10].

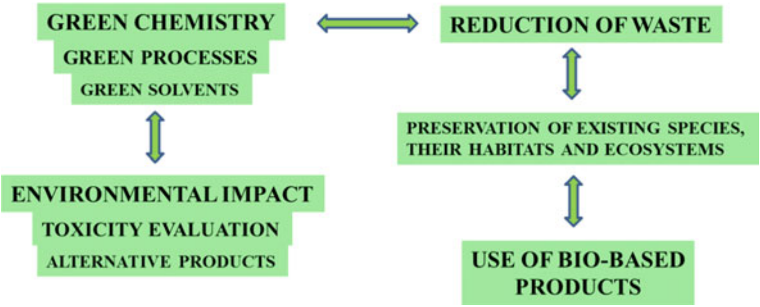


Fig. 4.1 Green chemistry as a whole

The aim of this chapter is to analyze the recent progresses in greener membrane materials and solvents used for the preparation of a sustainable polymeric membrane. Topics include an overview of membrane preparation techniques, as well as an analysis of production cost with an emphasis on membrane compounds such as solvents, green solvents, and polymers.

4.2 Techniques for Preparation of Polymeric Membranes

Phase inversion is the most diffused technique adopted for the preparation of polymeric membranes both at lab and industrial level. The word “phase inversion” indicates the transformation of a polymer solution from a liquid phase to a solid phase. It occurs because of a phase separation from a homogeneous starting solution induced by a temperature change, the use of a non-solvent or by the evaporation of the solvent contained in the polymer solution. Depending on the type of approach applied for the preparation of polymeric membranes different morphologies can be obtained [5].

Solvent evaporation represents the simplest approach for the preparation of polymeric membranes by phase inversion technique. It consists in dissolving the polymer in a solvent with a high volatility. A non-solvent can also be added to the dope solution. The solution is then cast on a proper support and the solvent is evaporated under controlled environment. The evaporation of the solvent generates the precipitation of the polymer and, depending on the presence and on the amount of the non-solvent, a membrane with a dense or porous structure can be obtained.

In wet cast process [known also as non-solvent induced phase separation (NIPS)] the polymer casting solution is immersed in a coagulation bath containing a non-solvent (generally water). The exchange between solvent and non-solvent takes place and it is responsible for the phase separation. Porous membranes, due to the solvent loss and counter diffusion of the non-solvent into the cast membrane, are, thus, obtained [11].

In thermally induced phase separation (TIPS), a polymer is dissolved at elevated temperature in a high boiling point solvent (called also diluent). The hot homogeneous polymer solution is then cast on a proper surface and is cooled down to let the precipitation of the polymer. The diluent is then removed, generally by solvent extraction, and porous microfiltration membranes are usually produced [12].

In vapor-induced phase separation (VIPS), upon a polymer solution is cast on the proper support, it is exposed to a vapor atmosphere containing a non-solvent (generally water) prior the immersion in a coagulation bath. Membranes formation occurs due to the diffusion of the non-solvent into the cast film leading to the formation of a porous membrane with no top layer.

4.3 Synthetic and Biopolymer Materials Used in Most Common Membrane Operations

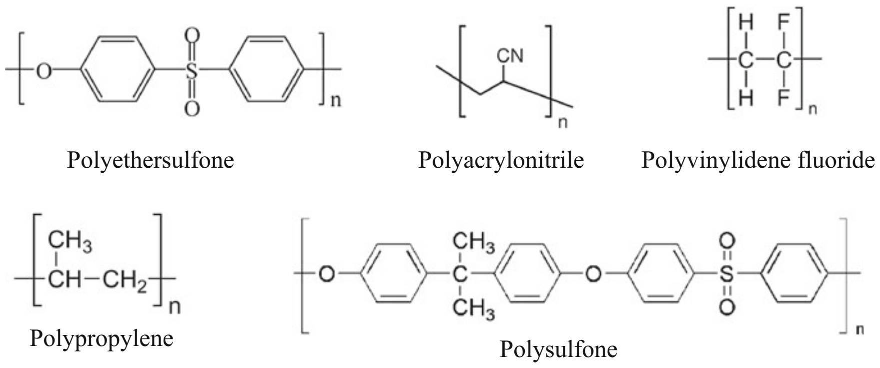
Membranes are currently commercially available for different processes such as desalination, water reuse, and ultra pure water production (reverse osmosis; RO), for hardness, heavy metals, and dissolved organic matter removal (nanofiltration; NF), for virus and colloid removal (ultrafiltration; UF) and for suspended solids, protozoa, and bacteria removal (microfiltration; MF) [4]. Most commonly used commercial NF, UF, and MF membrane materials are synthetic polymers. Polysulfone (PSU), polyethersulfone (PES), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polypropylene (PP), cellulose, and derivatives represent the most widely used current (first generation) organic membrane materials (Fig. 4.2) [1].

Herein, a brief overview of synthetic and biopolymer materials used to prepare membranes for water and wastewater treatment is reported.

Among the traditional polymers, the class of biopolymers is gaining an increasing attention for the preparation of membranes due to the possibility of using less toxic, environmentally friendly, and renewable materials. The stringent environmental regulations are also favoring the use of biopolymers and the development of new materials produced in a sustainable way [13]. Biopolymers can be obtained from different natural sources (microorganisms, plant, and animals) or chemically synthesized from biological starting materials (sugar, corn, starch, etc.).

Cellulose acetate (CA) is the most abundant biopolymer available on earth. It is a polysaccharide produced by the plants and, with its derivatives, is very well appreciated for the production of hydrophilic membranes mainly applied in water treatment and in biomedical field.

Among the biopolymers produced by bacteria, poly (lactic acid) (PLA), and polyhydroxyalkanohates (PHA) are among the most common materials used for membrane preparation. PLA is one of the most promising biopolymer with a great potential in replacing the conventional petroleum-based polymers. It is a thermoplastic polyester derived from lactic acid that is produced by the bacterial



Polyethersulfone

Polyacrylonitrile

Polyvinylidene fluoride

Polypropylene

Polysulfone

Fig. 4.2 Chemical structures of commonly used polymeric membrane materials fermentation of dextrose derived from plant starch. PHA are a class of polyester biopolymers derived from bacteria fermentation. They are a group of biodegradable polymers with a good biocompatibility. Polyhydroxybutyrate (PHB) and poly (hydroxybutyrate-cohydroxyvalerate) (PHBV) are the most important representatives of the class of PHA biopolymers.

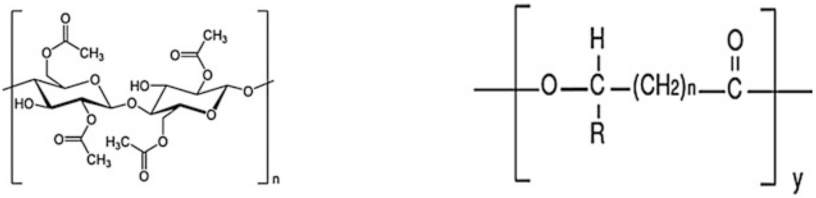
Chitosan (CHT) is the deacetylated form of chitin (Ch) produced by the outer shell of crustaceans. It is soluble in aqueous acidic solutions and is often applied in combination with other polymers for the production of membranes with adequate mechanical properties. Collagen is also a biopolymer derived from animals, and in particular from the connective tissue of the living organisms. Collagen and CHT due to their good biocompatibility have been widely applied so far in the preparation of membranes used for tissue regeneration. However, their hydrophilicity was also exploited in pervaporation (PV) and other water treatment membrane-based processes [14–17].

In Fig. 4.3, the chemical structures of the most used biopolymer materials in membranes are reported.

In the following section, the most common membrane operations in water and wastewater treatment are reported, highlighting the traditional polymers and biopolymers used as materials of the membranes applied in these processes.

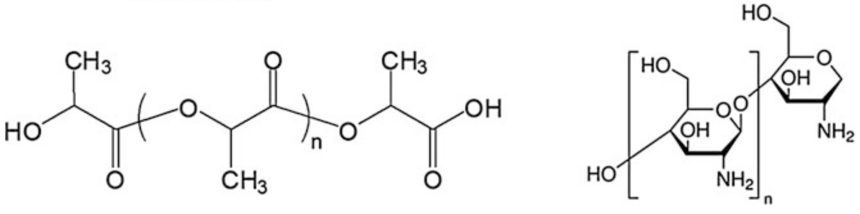
4.3.1 Reverse Osmosis (RO)

RO membranes are made of a dense or nonporous matrix (approx. 0.0001–0.001 μm) where the passage of molecules is allowed by cavities generated by the



Cellulose acetate

PHA



PLA

CHT

Fig. 4.3 Chemical structures of some of the most diffused biopolymers used for membrane preparation thermal motion of the polymer chains that form the membrane. Therefore, RO membranes selectively remove low molecular weight species such as inorganic solids (including salt ions, minerals, and metal ions) and organic molecules [1]. Over the past decades, the market share of RO process has witnessed continued domination in desalination and pure water production, when compared with other technologies [18, 19]. RO uses polymeric membranes called thin-film composite (TFC) structures comprised of a thin active layer (500 nm) supported on a porous substrate [20]. The support layer (usually a sulfone polymer) is itself a UF membrane with a thickness of 40–60 μm. The most commonly used polymeric membrane material for RO at present is polyamide (PA) [19]. Graphene, graphene oxide [21], zeolites [22], silica nanoparticles [23], polyhedral oligomeric silsesquioxane nanofiller [24], silver nanoparticles [25], carbon nanotubes [26] as nanomaterials have been recently tested for enhancing the water flux and salt rejection of RO polymer-based membranes. Recent insights on the integration of nanomaterials with polymer-based membranes have also revealed the antifouling properties of these nanoparticles [19, 27, 28].

Among biopolymers, cellulose triacetate and acetate are other polymeric membrane materials used for RO [29], but in this case they are used in form of thin hollow fibers. Although cellulose triacetate membranes are in a distant second position to PA TFC membranes in terms of market share, in recent applications, they are preferred because of their superior ability to withstand chlorine attack [19, 30]. The integration of commonly used polymeric materials such as CA and PA with other polymers or nanoparticles has ensured improvement in membrane performance by modifying the active layer to minimize the interfacial energy at the polymer–water interface [19].

The incorporation of hyperbranched polyesters into CA has also been tested for improved RO membrane performance. The reason for selecting hyperbranched polyesters is their hydrophilic nature. Addition of hyperbranched polyesters improved separation properties, wettability, and hydrophilicity of CA membranes [31]. It has also been reported that the integration of CA with polyvinyl alcohol could lead to improvement in CA RO membrane performance for desalination of seawater [32].

CHT was also used as a coating layer for the production of TFC PA membranes [17]. PA membranes were previously exposed to sodium hypochlorite solutions (for 30 and 60 min at the concentration of 1250 mg/L) and then to a CHT solution at different concentrations (for 60 min). The produced membranes presented higher hydrophilicity and lower contact angle. In particular, the TFC membranes prepared after exposure to a 1000 mg/L CHT solution for 60 min and to 1250 mg/L sodium hypochlorite for 30 min showed an important improvement in overall flux up to 2.5 times and an increase in salts rejection (from 92 to 95% for NaCl and from 86.36 to 95.06 for $MgCl_2$) in comparison to the pristine membrane.

4.3.2 Nanofiltration (NF)

NF membranes exhibit performance between RO and UF membranes, and they were also called "loose RO membranes". NF membranes can separate species ranging from 0.001 to 0.01 μm in size. This includes most organic molecules, viruses, and a range of salts. Further, NF membranes can reject divalent ions, so NF is often used to soften hard water [1, 33]. There are a number of commercially available NF membranes in the market. Among the most widely used is the TFC-NF membrane. Its excellent permeability and selectivity over asymmetric NF membranes offered competitive improvement of this kind of membrane [34, 35].

The currently available TFC-NF membranes are mainly prepared by forming a very thin PA active layer on the microporous support mainly prepared from PSU or PES [36, 37]. These materials (i.e., PSU and PES) exhibit excellent permeability, selectivity of permeate, mechanical stability, and chemical resistance [1]. Microporous support layer for TFC may be also prepared from polyether ketones, PVDF, sulfonated PVDF, or PAN [1, 38]. The substrate membrane is commonly prepared through a dry–wet phase inversion technique, while the top active layer is formed via the interfacial polymerization procedure [34].

Preparation of a NF composite membrane has been reported via the interfacial polymerization of piperazine (PIP; a type of PA) with trimesoyl chloride on the surfaces of microporous polyacrylonitrile (PAN) supports to form a strong interaction between the active and support layers [39]. Interestingly, the functional groups of –CN in PAN support could be modified to be –COOH groups through a simple treatment with NaOH solution at ambient temperature. The results indicated that the membrane surface roughness increased significantly with increasing the modified PAN concentration [39].

Verisimmo et al. [40] used PAs such as PIP, *N,N*-diaminopiperazine, 1,4-bis (3-aminopropyl)-piperazine) and *N*-(2-aminoethyl)-piperazine to react with trimesoyl chloride separately during composite membrane preparation. Among these membranes, it was reported that PIP—trimesoyl chloride exhibited higher water permeability and rejection of monovalent and divalent salts than those of other membranes. This may be the reason for an increase in the use of PIP for commercial membranes. The use of electrospun membranes, as a support layer for desalination, has been reviewed by Subramanian et al. [41].

Aquaporin, a highly selective water channel protein, has received worldwide for water reuse and desalination attention because of its potential to form biomimetic membranes with high flux and rejection. Aquaporin is a bidirectional water channel protein present in cell membranes, and it regulates the flow of water in and out of cells. Aquaporin has, therefore, a potential to improve the water flux through incorporation into synthetic polymeric membranes. Incorporation of purified aquaporins into the active layer of the polybenzimidazole NF membrane has been reported [42]. It was found that membranes modified with Aquaporin displayed lower flux declines and higher flux recoveries as compared to unmodified polybenzimidazole membranes [42].

Among the biopolymers, cellulose and its derivatives, such as carboxymethyl cellulose (CMC), have been extensively used for the preparation of NF membranes [43, 44]. These membranes, however, can have the limitation of poor permeate flux even if they present a good salt rejection. In order to overcome this problem, Shao et al. [45] introduced strong acid groups such as sulfate groups in CMC able to improve the hydrophilicity and consequently enhance the permeate water flux.

CA was used by Su et al. [46] for the preparation of NF hollow fiber membranes to be applied in forward osmosis (FO). CA membranes obtained by heat-treating after phase inversion the spun hollow fibers with hot water (at 60 °C for 60 min and 95 °C for 20 min followed by a rapid cooling with cold water) presented the most suitable properties in terms of pore diameter (0.30 nm). Using a $MgCl_2$ draw solution, the water flux was 7.3 L/m^2 h with a salt leakage of 0.53 g/m^2 h.

4.3.3 Microfiltration (MF) and Ultrafiltration (UF)

Porous polymeric membranes (i.e., MF and UF) were applied to various water treatment processes, including water and wastewater filtration and as pretreatment for NF or RO membranes [4, 47]. UF and MF membranes are often prepared from the same materials, but preparation methods are different to allow tailoring the pore sizes and morphologies [1].

CA was one of the first polymers employed, thanks to the invention of the Loeb–Sourirajan asymmetric membrane in the 1960s [48], and it is still used to form membranes with properties ranging from MF to RO [1, 49]. CA is hydrophilic and produces smooth membrane surfaces with low fouling propensity [50]. Cellulosic membranes are also relatively easy to prepare with a wide range of pore sizes and are relatively inexpensive.

Disadvantages of CA include limited temperature range (less than 30 °C) and pH range (4–6). More alkaline conditions and temperatures higher than 30 °C accelerate the rate of hydrolysis causing degradation of the polymer. Due to the cellulose backbone, CA membranes are also biodegradable and can, in fact, be consumed by organisms growing in biofilms [1, 38, 51].

Other more widely useable MF and UF membrane polymers comprise PS, PES, PVDF, PP and PAN. These polymers demonstrate excellent permeability, selectivity, and stability in water treatment applications [1, 52].

The use of biopolymers MF and UF is documented in the literature, where PLA and CA with its derivatives are the most important exponents.

UF hollow fiber membranes were produced by Moriya et al. by phase inversion technique and using PLA as a polymer and DMSO as a solvent [53]. The effect of polyethylene glycol (PEG) as a pore forming agent (from 0 to 15 wt% as range of concentration) on the membrane morphology was also evaluated. Hollow fibers prepared with 15 wt% of PEG presented the most porous structure due to suppression of PLA crystallization as a consequence of dope viscosity increase. The water permeability of PLA membranes was found to increase (from about 400 to 1100 L/m^2 h bar), as expected, by increasing PEG concentration although the tensile strength decreased. The bovine serum albumin (BSA) rejection was constant (about 80%) for all the PLA membranes evaluated (without and with PEG) excluding the hollow fiber containing the higher PEG concentration (15 wt%) which showed a drop in BSA rejection to 55.8%.

Water filtration hollow fiber membranes in CA produced by electrospinning and coated with chitin nanoparticles were realized by Goetz et al. [54] as shown in Fig. 4.4. Ch nanocrystals (ChNC) are known for their antifungal and antimicrobial properties together with a large surface area and good mechanical properties. It was observed from the results that ChNC did not influence the water permeability of the original CA membranes locating the produced membranes in the range of MF. The CA membranes prepared with Ch showed also improved anti-biofouling properties and reduced the abiotic fouling formation. Moreover, the ChNC turned the pristine hydrophobic membrane into a super-hydrophilic surface (contact angle of 0°).

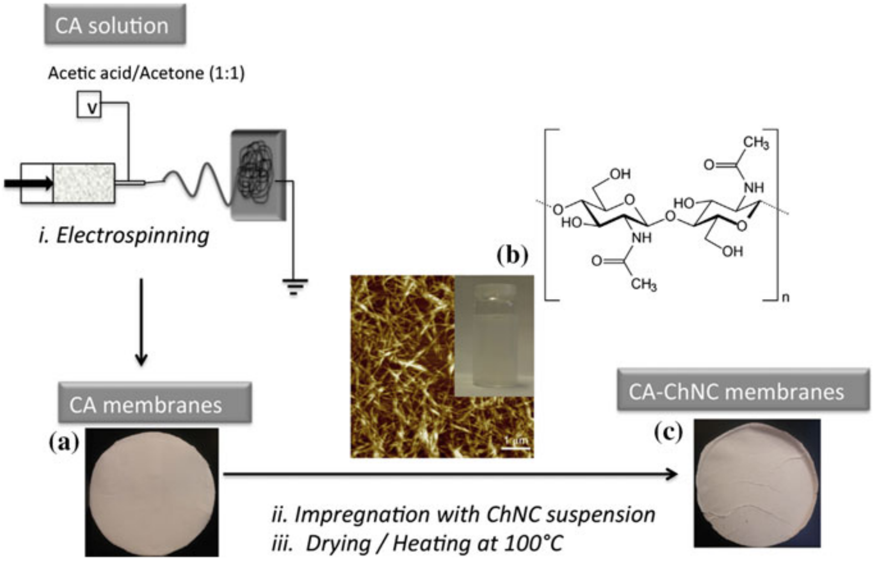


Fig. 4.4 Scheme showing the methods and materials involved in the membrane processing and functionalization. (*i*) Electrospinning of CA mats, (*ii*) impregnation of CA mats and (*iii*) drying and heating of the impregnated mats are the process steps. **a** Electrospun CA mat, **b** ChNC used for impregnation (photo of the ChNC suspension, the AFM image of nanocrystals and the chemical structure of Ch) and **c** the CA-ChNC membrane mat obtained after impregnation are shown [54]. Reprinted with the permission from Ref. [54]. Copyright 2016 Elsevier

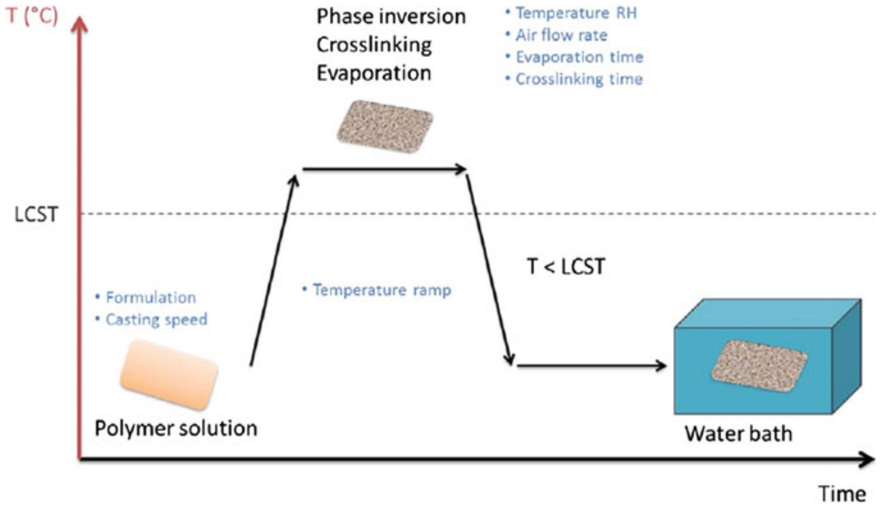


Fig. 4.5 Membrane preparation procedure based on the LCST-TIPS method. Reprinted with the permission from Ref. [9]. Copyright 2017 Elsevier

A strong improvement toward the green membrane preparation should be given by the use of renewable bio-sourced materials as polymers. In this respect, Hanafia et al. [9] illustrated as a renewable, non-toxic, cellulose-derivate polymer, e.g., hydroxypropylcellulose (HPC) should be efficiently used as polymer for making porous membranes suitable for water treatment. Moreover, since the polymer is soluble in water, no hazard solvent was used in the membrane preparation procedure. Membranes were prepared through a phase inversion process based on the HPC lower critical solution temperature (LCST) coupled with the TIPS as shown in Fig. 4.5.

This work demonstrated as membrane technology advancing fast in the direction of the green and sustainable chemistry principles.

4.3.4 *Pervaporation (PV)*

PV is a membrane process based on the removal of one or two components contained in a feed solution by using a dense membrane. The membrane acts, therefore, as a selective barrier between a liquid binary or multicomponent mixture that has to be treated and a permeate vapor phase. In PV, the driving force is represented by the chemical potential gradient between the two sides of the membrane that can be induced by adopting different approaches: (1) using an inert gas at the permeate side; (2) applying a temperature difference between the two sides of the membrane; (3) applying a vacuum on the permeate side [55]. The preferential separation of one component respect to the other is regulated by the chemical–physical interactions established between the target component and the membrane material. PV received an increasing attention during the last decades due to the possibility to operate at mild conditions, with a low energy consumption, a low environmental impact and achieving, at the same time, high selectivity. PV is mainly applied for the separation of azeotropic solutions and close boiling mixtures due to its competitiveness respect to distillation and evaporation that are energy intensive processes. However, due to the development of novel and more and more performing materials, PV, is very well appreciated also for the separation of organic–organic mixtures and for the removal of volatile organic compounds (VOCs) from aqueous solutions.

On the basis of the separation that has to be achieved, different polymers (hydrophilic or hydrophobic) need to be used. Polydimethylosiloxane (PDMS) thanks to its stability and high hydrophobicity is one of the most studied polymers in PV. Silicate filled and unfilled PDMS membranes were prepared, for instance, by Dobrak et al. [56] for the pervaporative separation of ethanol/water mixtures by varying the alcohol concentration in the feed and the operating temperature. Filled membranes presented a higher total flux in comparison to pristine PDMS ones which increased with the increasing of ethanol concentration in the feed solution (from 3 to 9 wt%). In particular, the highest increase in total flux was observed for the silicalite 1-filled membrane which presented (at 41 °C) an increase of about 45% (from about 170 to about 250 g/m^2 h) respect to the unfilled membrane that showed the lowest increase (about 25%) at the same temperature (from about 120 to about 140 g/m^2 h). Regarding the selectivity, membranes prepared with commercial ZSM-5 fillers (CBV 3002) fillers presented, at all investigated ethanol concentrations and temperatures, the highest values respect to the silicalite 1-filled membrane and the PDMS unfilled one, reaching a selectivity of almost 7 at 3 wt% ethanol concentration and 61 °C.

Biopolymers have also been successfully applied in PV in several types of separations. Lin et al. applied CHT/konjac glucomannan gum (KGM) for the dehydration of caprolactam (CPL) solution [15]. KGM is a natural polysaccharide derived from konjac tuber and used as a modifier to be incorporated into CHT membranes. The results demonstrated an increase in membrane selectivity for the novel CHT/KGM membranes in comparison to the traditional PVA and PVA/CHT membranes generally adopted for this type of separation with a maximum value of selectivity of more than 8000 at 40 °C with a 60 wt% CPL solution.

The use of biopolymers in PV is very well documented in literature for different types of separations: *n*-methyl-2-pyrrolidone/water [57]; benzene/cyclohexane [58]; Methanol/MTBE [59]; ethanol/water [60]; *t*-butanol/water [61].

4.4 Traditional Solvent and "Newer" Non-toxic Solvents in Membrane Preparation

The need for chemicals design that fulfill the green and sustainable concepts has attracted more and more attention over the past decades and has reflected the regulations restricting progress which is strongly related to the more and more in-depth knowledge on the hazard effect of chemical compounds [8, 10]. This novel concept of chemistry has radically changed the chemical plants engineering and the environmental problem solving approach, for the preservation of multiple species protection and the protection of their habitats and overall biodiversity in the first place [62–64]. Among the compounds used in chemical processes, solvent is, reflecting its definition, "the one present in larger quantity" [65]. This implies that the solvent safety is a decisive factor in the near-future chemistry and that, the total feasibility of an ideal chemical process will be determined not only by the environmental and economic sustainability, but also by the total absence of harmful effects of the employed materials on human health. Membrane technology, which is strictly correlated with the concept of process intensification, is perfectly framed in the green chemistry context and it should offer tremendous potential for the substitution of the traditional separation processes [66–70]. However, membranes prepared via phase inversion method, generally are obtained by dissolving the selected polymer in a highly toxic solvents, e.g., *N*-Methyl-2-pyrrolidone (NMP), *N,N*-Dimethylformamide (DMF), *N,N*-Dimethylacetamide (DMA) and phthalates [71–75].

These diluents pose severe risks for the workers' safety and the environment, thus a more sustainable production process is needed [76]. Interestingly, less toxic, or completely green, new solvents, have been recently synthesized and/or experimented for the substitution of the hazard ones for the preparation of polymeric membranes mainly made of PVDF, PES, cellulose-derivates [10]. The properties that have the greatest impact on the entire production process are, undoubtedly, in addition to the solvent capacity and the (eco)toxicological profile, the miscibility with water (which is widely used as a coagulation bath during the phase inversion procedure) and the boiling point of the selected diluent. The most appropriate alternative is, if there is, a bio-based solvent originating from renewable feedstocks [77]. Methyl- and ethyl-lactate, esters formed from lactic acid and methanol and ethanol, respectively, represent promising solvents for membrane preparation [10, 78, 79]. In accordance with the Green Chemistry principles, these two diluents are synthetized from lactic acid, which is an emerging building block for the production chain of next-generation biodegradable plastics and solvents [78]. Medina-Gonzalez et al. [78] reported the CA membrane preparation by using methyl lactate as solvent and LiCl as pore former agent for UF applications. The promising results are in terms of pure water permeability in particular if it is compared with those obtained with commercial UF CA membranes (Table 4.1).

Medina-Gonzales and Remigy [79] studied also the CA membrane production by using ethyl lactate as bio-based green solvent [80, 81]. In this case, membranes with a pore size in the UF-MF range (0.1 μm) were prepared employing 20 wt% CA, 3 wt% $CaCl_2$ and 9 wt% water as additives.

In recent years, growing attention has been paid also to the methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate, commercially available as Rhodiasolv®Polarclean [82–84, 88], named in this chapter as Polarclean®. In Fig. 4.6 the molecular structure of Polarclean® is reported.

Table 4.1 Molecular weight cut-off (MWCO) and pure water permeability (PWP) of the handmade [78] and commercial Sterlitech UF CQ (GE Osmonics) CA membranes

Membrane	Polymer content (wt %)	LiCl content (wt%)	Methyl lactate content (wt%)	MWCO (PEG KDa)	PWP (L/m^{2}h bar)
Handmade	20	6	64	20	23.0
Commercial	–	–	–	20	10.2

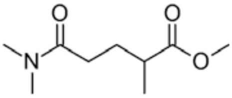


Fig. 4.6 Molecular structure of methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate (Polarclean®)

This novel polar solvent is eco-friendly and water soluble; it demonstrated excellent solvency capability for both amorphous and semicrystalline polymers, such as polysulfones [82] and PVDF [84, 85], respectively. Moore et al. described the PES membrane preparation via NIPS by casting dope solution composed of 16 wt% polymer and using PVP as pore former additive [82]. Hassankiadeh et al. [85] employed Polarclean® for the PVDF hollow fiber membrane preparation, examining the influence of the pore former and the coagulation bath temperature on the membrane morphology and performance. Dope solution composed of PVDF/glycerol/Polarclean® system led to membrane with good mechanical features and porosity. Sanguineti et al. described the procedure for producing PVDF hollow fiber by using Polarclean® via spinning process [86]. Polarclean® was proposed by Jung et al. to fabricate microporous PVDF membranes via phase inversion [84]. In this case, interesting results were registered by using Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic®) as additive, which allowed the production of porous, highly permeable PVDF membranes having narrow pore size distribution, as shown in Fig. 4.7.

Also citrate esters, such as acetyltributylcitrate (ATBC) [87, 88], acetyltriethylcitrate (ATEC) and triethyl citrate (TEC) [87] were investigated as alternative solvents for PVDF, showing the possibility to obtain porous membranes suitable for MF applications. Diethylene glycol monoethyl ether acetate (DCAC) [89], glycerol triacetate (Triacetin) [90], as well as triethylene glycol diacetate (TEGDA) [91] and triethyl phosphate (TEP) were also proposed as viable substituents to the toxic commonly used solvents for both PVDF flat sheet [92], and hollow fiber membrane preparation. TEP was investigated by Fadhil et al. to prepare (poly vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP) hydrophobic porous membranes for membrane distillation operations, evidencing also in this case as less-toxic solvents can replace hazard chemicals in membrane preparation for water treatment [93]. The authors reported good results in terms of membrane permeation (16 kg/h m^2)

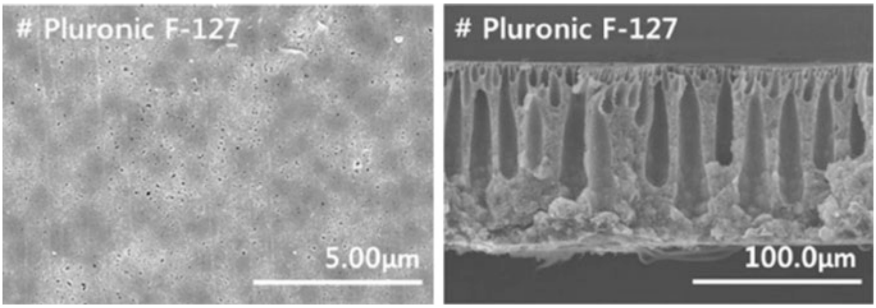


Fig. 4.7 SEM images (on the *left* surface and on the *right* cross-section) of the PVDF membranes prepared by Jung et al. by using Polarclean® as sustainable solvent and Pluronic as additive. Reprinted with the permission from Ref. [84]. Copyright 2016 Elsevier

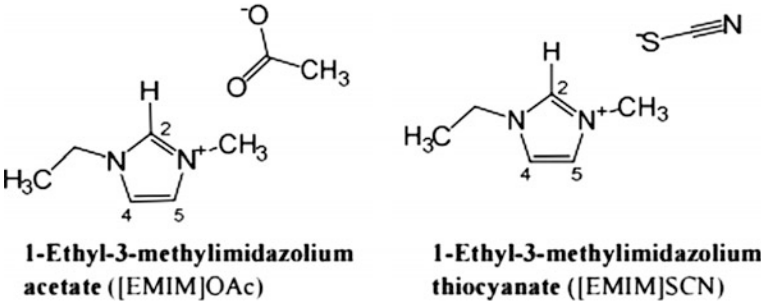


Fig. 4.8 Molecular structure of ([EMIM]OAc and ([BMIM]SCN ILs used as less-toxic solvents for CA membrane preparation by Xing et al. Reprinted with the permission from Ref. [96]. Copyright 2016 American Chemical Society

and salt rejection (99.3%) after membrane distillation experiments, using the membrane prepared with 12 wt% P(VDF-HFP) in TEP and coagulated in an alcohol-water bath. Another emerging class of alternative solvents comprises ionic liquids (ILs), even if not all the members of the ILs family can be defined as low or non-toxic [10]. Among the most attractive ILs, because of their complete miscibility with water, 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) and 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN) were employed by Xing et al. [94, 95] for producing CA membranes via phase inversion. The prepared membranes showed distinguished structure and properties in terms of UF performance in comparison to those obtained with commonly used phase inversion diluents, such as NMP and acetone. Recently, Xing et al. also studied the molecular interactions of CA chains and the selected 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) and 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) ILs [96], as shown in Fig. 4.8.

Also supercritical fluids have attracted interest for the liquid non-solvent replacement during phase inversion. In particular, supercritical carbon dioxide

$ScCO_2$ (P_c = 7.21 MPa and T_c = 31.1 °C) has been employed because it is economically advantageous, safe, and easily available and consents to operate at low temperatures and relatively low pressures [97]. The greatest advantage in using $ScCO_2$ lies in recovering the liquid solvent dissolved in $ScCO_2$ through a depressurization step by using a separator placed downstream of the membrane fabrication apparatus [97].

Reverchon and Cardea reported the study on CA membrane preparation by using acetone as solvent and $ScCO_2$ as non-solvent [98]. They investigated the effect of polymer content (5–40 wt%) and supercritical CO_2 properties, i.e., temperature and pressure on the final membrane morphology. Membrane structure changed from beads-like to cellular when the polymer concentration in the dope solution increased, and temperature and pressure were fixed at 45 °C and 200 bar, respectively. The first one morphology may be promoted by nucleation and growth of polymer droplets and the subsequent solidification of the polymer rich phase, while the cellular structure derived from the growth of droplets of the lean phase. The change of CO_2 temperature (45 or 65 °C) revealed that this parameter was not determinant in the membrane formation. On the contrary, CO_2 pressure played a crucial role during phase inversion. In fact, at 100 bar (and 45 °C) a continuous surface was observed when the polymer was used in the range between 15 and 40 wt%, whereas beads-like elements were obtained when lower polymer content were used (5 and 10 wt%). The authors attributed these changes to the lower solvent power exhibited by CO_2 at 100 bar, which delayed the demixing process.

4.5 Costs of Membrane Production: A Case Study of Polymeric Hollow Fibers

4.5.1 Spinning Process of Hollow Fiber Membranes and Assumptions

Spinning of hollow fiber can be schematically described as in Fig. 4.9. By mixing polymer with solvent and additive, a homogeneous polymer dope is extruded via a spinneret; after phase separation either by thermal gradient or immersion precipitation (the process in the Fig. 4.9 shows only the immersion precipitation phase separation), the solidified fibers are collected, rinsed, dried. Module production is a follow-up which involved multi-step processes, and is out of the discussion in this session.

For the sake of brevity, we assume the following simplified main parameters for the evaluation of the cost for preparation of hollow fiber membranes, as reported in Table 4.2. A full-scale production line for annual productivity of 1 million square meter membranes is assumed to be a standard unit. All other cost issues are based on the contemporary cost from China, such as the electricity, water, manpower, and rental. The cost for the production line is high, but in average to the annual

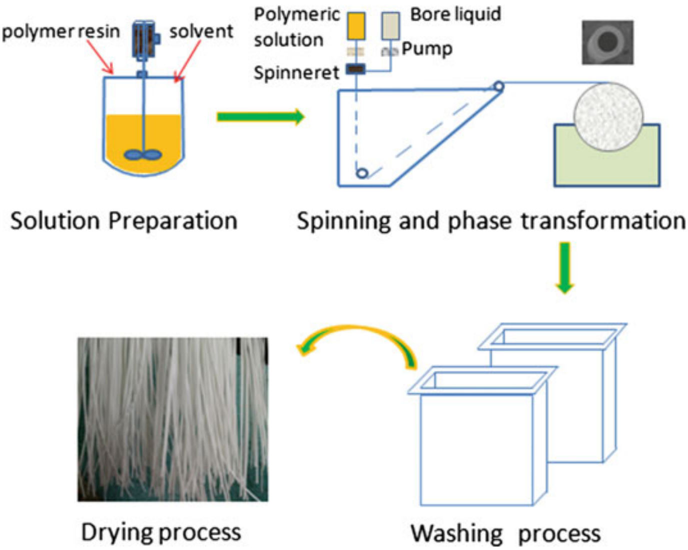


Fig. 4.9 Schematic of spinning process of hollow fiber membranes. The process ends at the membrane preparation and the module production part is skipped

productivity, the amortization based on unit membrane (in m^2) is comparably low, as shown in Fig. 4.10.

Figure 4.10 shows the effect of the solvent cost on the cost index of membrane. A linear relationship between the cost of the membranes and the solvent cost exists. Obviously, the solvent recovery reduces the membrane production cost significantly when the solvent price is high. However, at low solvent price, the cost of the hollow fiber membranes produced without solvent recovery is slightly higher than the cost of those produced with solvent recovery system. When using solvent recovery system, additional amortization and the electricity are added up to the total cost. At low solvent price, the cost of the membrane is slightly lower without solvent recovery system, due to the unbalanced cost of depreciation of the investment and slight higher energy consumption. A break-even point is at the solvent price of 0.76 €/kg. However, market price for the solvent is above this value, this means that adoption of the solvent recovery system is economically beneficial for a full-scale manufacturing plant for membranes.

In Fig. 4.11, the cost breakdown for the hollow fiber membranes is reported. The polymer is the major cost issue for making the membranes, because of the high polymer price. Without solvent recovery, it is obvious that the cost of solvent is high as the solvent prices changes from 2 to 5€. However, the solvent recovery system gives strong impact on the percentages of the cost of the solvent. It is therefore recommended to reuse the solvent for the benefit of environment as well as the profit. However, it should be noted that the installation of solvent recovery system also depends on the production scale. Detailed economic analysis is

Table 4.2 Assumptions for estimation of the cost for preparing hollow fiber membranes

Parameters	Values	Unit	Notes
Production capacity	1,000,000	m^2/year	Inner diameter = 0.8 mm; outer diameter = 1.3 mm; porosity = 80%; consider 2.5 m^2 corresponds to about 1 km length of hollow fiber; assume 10% waste in materials; this is a typical industrial scale production line.
Working days per year	300	days	Every day 24 h
Dope composition: polymer/solvent/additive	20/70/10	wt%	Just for simplicity; specific dope composition may influence the exact value of the membrane cost, but does not change the conclusion of this report
Cost of the polymer resins	20	€/kg	The average cost of PES
Cost of electricity	0.135	€/kWh	Base on Chinese tariff; average electricity tariff = 1 Yuan; average working days per year = 264 days; average electricity per day = 10,000 kWh
Cost of water	0.676	€/m^3	Base on Chinese tariff; average electricity tariff = 5 Yuan
Cost of manpower	0.319	M €	24 full time employee including, average salary 13.3 K/year
Spinning machine	2.16	M €	Assume the cost of a full-scale production line of 1 million square meters; amortization is based on 10 years
Solvent recovery system	1.08	M €	Market value for full-scale production line; amortization for 10 years; the loss of solvent is assumed to be 10%

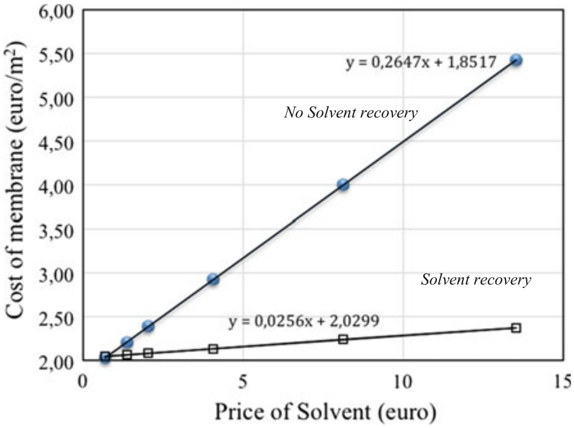


Fig. 4.10 Effect of the solvent cost on the production cost of membrane. Assumptions are listed in Table 4.2

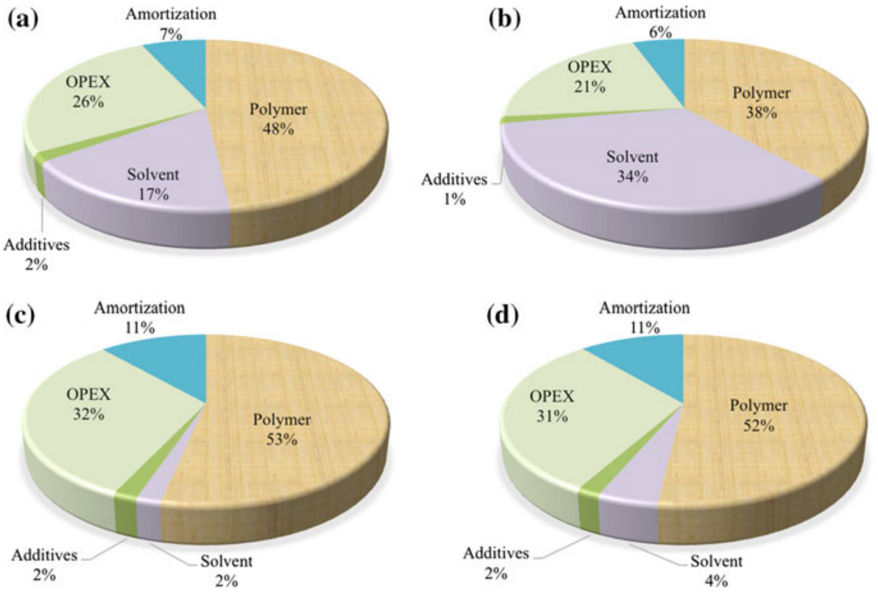


Fig. 4.11 The distribution of the cost breakdown for four typical cases: **a/b** without solvent recovery; **a** solvent price 2€; **b** solvent price 5€; **c/d** with solvent recovery; **c** solvent price 2€; **d** solvent price 5€. OPEX: operational expenses including the power, water, manpower and rental

required before any investment decision being made. Very interesting phenomenon is that in case of solvent recovery, the percentage of the OPEX appears to be high. This result indicates that further reduction of the cost for membrane is then to optimize the process.

4.6 Conclusion and Future Outlook

Sustainability is defined as the quality of a sustainable development compatible with the safeguard of the environment and able to support, respect and defend the life cycle and the natural resources. In this context, membranes and the processes related to them play an important and crucial role. Membrane filtration, for instance, is experiencing an exponential growth in water treatment applications (UF, MF, NF, and RO) for its ability to separate a large variety of contaminants, to reduce the energy consumption, allowing, at the same time, to obtain a high quality filtrate. A plethora of polymeric materials are nowadays available for the fabrication of membranes. Among the traditional polymers, however, in the optic of using more sustainable materials, the biopolymers can represent a valid and concrete alternative for the fabrication of sustainable membranes. CHT, CA, PHA, and PLA are just some of the most diffused biopolymers, which are currently and successfully used for the preparation of membranes applied in different areas but still only at lab scale level.

A complete sustainable fabrication method, however, implies not only the use of biopolymers but also the possibility to adopt less toxic or completely green solvents able to replace the more hazardous and toxic ones traditionally used for polymer solubilization. Polarclean®, TEP, DMSO, $ScCO_2$, ATBC, ATEC, TEC are among the family of more eco-compatible solvents reported in the literature and applied in membrane preparation at lab scale level too.

Membrane technology is already regarded and considered as a sustainable process. For this reason, the possibility to combine the sustainable process with sustainable membrane fabrication methods by means of biopolymers and green solvents, represent one the challenge for the next future in the framework of meeting the more stringent environmental regulations for natural resources preservation.

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Chapter 5
Inorganic Membranes in Water and Wastewater Treatment

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Abstract Worldwide water scarcity and an increase in population growth have become unprecedented urgent global issues. There is a pressing need to develop robust membrane technologies for water and wastewater treatment at lower cost. Inorganic membranes feature superior chemical, thermal, and mechanical robustness as well as reusability. They are ideally suited for harsh environments in many wastewater treatment applications. Common fabrication methods of inorganic membranes include slip casting, tape casting, pressing, extrusion, dip coating, sol-gel process, atomic layer deposition, and thermal spray. For the fabrication of inorganic hollow fiber membranes, the combination of phase inversion and sintering is used. The excellent packing density and high specific area of inorganic hollow fiber membranes can offer great treatment capacities for large-scale applications. Commercial inorganic membranes have been applied in a wide variety of industrial applications and to compete with polymeric counterparts on a whole-life cost basis. Recent progress in inorganic membrane science and technologies have shown great potential in many water treatment applications, including potable water production, desalination, wastewater treatment, as well as juice clarification and concentration.

Keywords Inorganic membranes · Pressure-driven membrane processes · Membrane distillation · Preparation of inorganic membranes · Thermal spray · Inorganic hollow fiber membranes · Potable water production · Desalination · Wastewater treatment · Juice clarification and concentration

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5.1 Introduction

5.1.1 Water and Wastewater Treatment

Water sustains human life and its purity cannot be compromised at any cost. Although water is the most abundant resource on earth, increasing shortage of clean water has become a pervasive problem throughout the world. Water scarcity affects more than 40% of the global population. It is estimated that 783 million people do not have access to clean water and over 1.7 billion people live in river basins where water use exceeds recharge [1]. Besides, the increase in expectations for water quality and the requirements of selective separation with high purity have driven the developments of membrane technology in water and wastewater treatment. Compared to conventional water treatment processes, membrane technologies are at lower cost and with less energy, while at the same time minimizing the negative impacts on environment.

5.1.2 Inorganic Membranes

Membranes are categorized into two main segments, inorganic and organic membranes. Organic membranes are primarily polymeric membranes that presently dominate the membrane market. Inorganic membranes can be further classified into ceramic and metallic membranes. Materials of inorganic membranes include oxide mixtures and sintered metals. Inorganic membranes have received considerable attention due to their superior chemical, thermal, and mechanical stability. They are, therefore, ideal candidates for harsh water purification processes, such as industrial wastewater treatment and oil/water separations [2]. Flux through inorganic membranes is more easily recovered after fouling because they can withstand harsh chemical and thermal cleaning methods, as well as backwashing with high velocities [3]. Besides, ultrasonic technology provides an alternative way for membrane cleaning and fouling control [4–7]. Ultrasonic transducer generates an acoustic shock wave into the medium, creating cavitation bubbles to remove foulants. In the past 30 years, inorganic membranes have been rapidly developed, with the number of published articles increasing from 474 in 1985 to 3682 in 2016 (Fig. 5.1). The ceramic membranes market is projected to reach a market size of USD 6245.1 million by 2020. It is estimated to reach the CAGR of 11.96% between 2015 and 2020, higher than the CAGR of 8.74% in the polymeric membranes market.

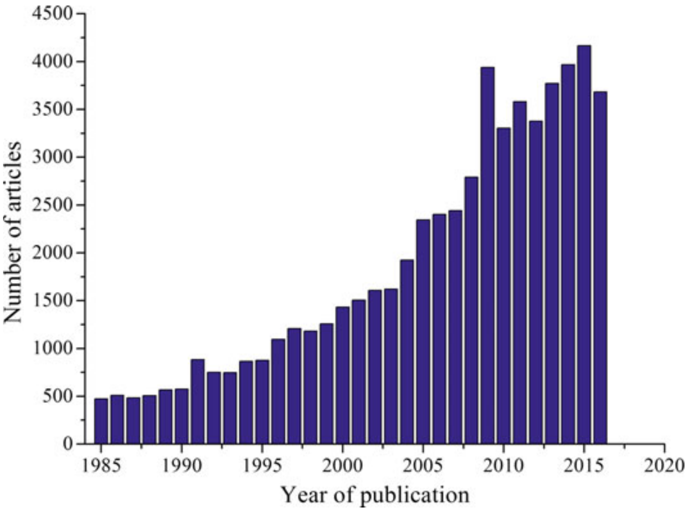


Fig. 5.1 Number of published articles from the year of 1985–2016

5.2 Membrane Processes in Water and Wastewater Treatment

5.2.1 Pressure-Driven Membrane Processes

In a pressure-driven membrane process, a feed stream is separated by a membrane into a retentate and a permeate. The pressure difference between the feed and the permeate sides acts as the driving force to transport the solvent through the membrane. The pressure-driven membrane processes can be classified by membrane pore size, size, and charge of the retained substances. Figure 5.2 shows the membrane filtration spectrum that distinguishes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [8].

Microfiltration (MF) membranes have a pore size around 0.1 µm. They are generally applied to separate the microorganisms in drinking water. Besides, they can be used in various applications such as solid–liquid separation, separation of oil/water emulsions, beverage and pharmaceuticals industries, biological wastewater treatment, and as pre-filters to remove particles that may cause problems in further treatment steps. Ultrafiltration (UF) membranes have a pore size around 0.01 µm. UF involves removal of suspended solids, viruses, bacteria, and high concentrations of macromolecules. UF applications include oil–water separation, fruit juice clarification, milk and whey production, purification of pharmaceuticals, potable water production, and secondary or tertiary wastewater reuse. For the MF and UF processes in which membranes generally consist of spherical particles, the membrane flux can be described by Kozeny–Carman's law:

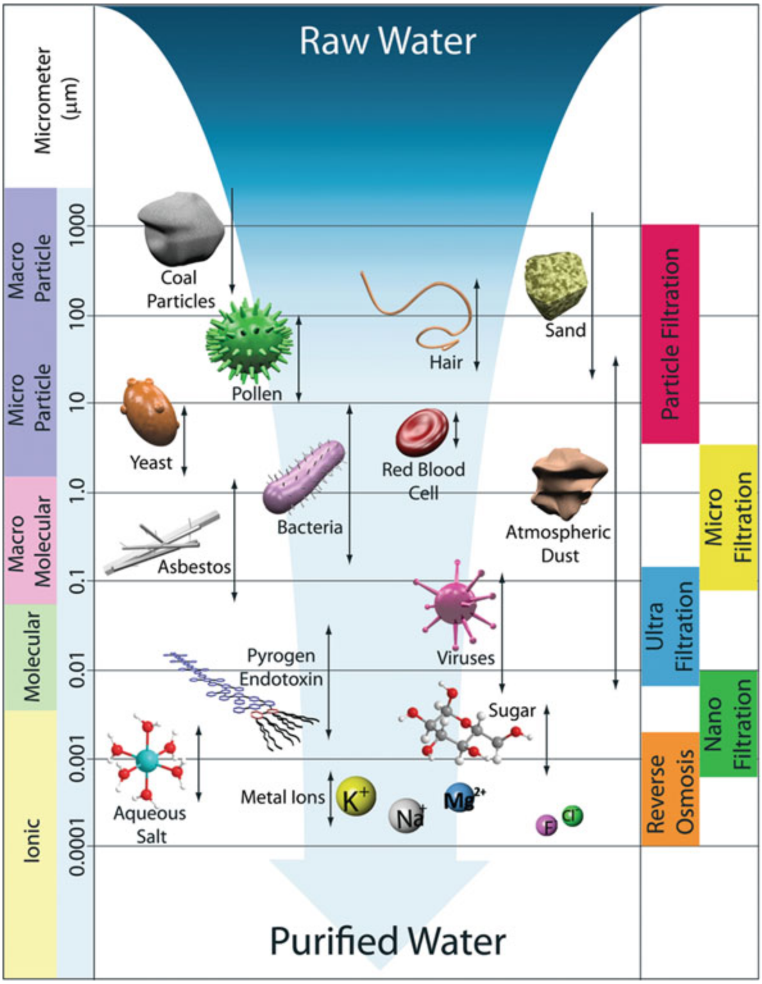


Fig. 5.2 Schematic diagram of the membrane filtration spectrum [9] (Reprinted from Lee et al. (2016), with permission from Royal Society of Chemistry)

$$J = \frac{\varepsilon^3}{K\eta S^2(1-\varepsilon)^2}\frac{\Delta P}{\Delta x}$$

where J is the membrane flux (m^3/m^2-s), K is the Carman–Kozeny constant, ε is the porosity, S is the specific surface area (m^2/m^3), η is the permeate viscosity (Pa-s), ΔP is the pressure difference (Pa), and Δx is the membrane thickness (m).

The pore size of a nanofiltration (NF) membrane is typically around 1 nm, which corresponds to dissolved compounds with a molecular weight of about 300 Da. NF processes remove most organic molecules, nearly all viruses and a range of salts.

Monovalent ions can pass freely through the membrane, but highly charged multivalent salts and low molecular weight organics are rejected to a much greater degree. In water treatment processes, NF membranes are used for hard water softening and color removal. Reverse osmosis (RO) membranes have a pore size of around 0.1 nm. RO is a high-pressure and energy-efficient process that removes most minerals and monovalent ions in water. RO processes have been applied in seawater desalination, fruit juice concentration, cheese whey concentration, ice-making, and car wash water reclamation. In these applications, the goal is either to reduce the wastewater for disposal or to retain the components of the feed stream as the product.

5.2.2 Thermally Driven Membrane Process

Membrane distillation (MD) is a thermally driven process driven by the vapor pressure difference existing between both sides of a hydrophobic porous membrane. MD has relatively low operating temperature compared to conventional processes, and the hydrostatic pressure encountered in MD is lower than that used in pressure-driven membrane processes like RO [10]. Besides, MD can be partially powered by alternative energy sources, such as solar energy, waste heat and geothermal energy. The aqueous permeate can be in direct contact with the membrane, which is called direct contact membrane distillation (DCMD). Alternatively, the water vapor of hot feed can be collected in different manners on the permeate side, such as air gap membrane distillation (AGMD), vacuum membrane distillation (VMD), and sweeping gas membrane distillation (SGMD) [11]. The four different configurations of membrane distillation are illustrated in Fig. 5.3. MD processes have been applied successfully in various fields, such as seawater desalination [12, 13], removal of heavy metals in wastewater [14], and juice concentration [15, 16].

In a typical MD process, vapor transport across a membrane can be defined by

$$f = K(T) \times \left(\frac{r \times \varepsilon}{\tau \times b}\right)^{\alpha}$$

where f is the permeance of the membrane, $K(T)$ is a function of temperature and molecular weight of the gas, r is the average radius of the membrane pores, ε is the membrane porosity, τ is the tortuosity of the membrane, and b is the membrane thickness. The value of α varies with the types of permeation regime under which vapor permeates across the porous membrane [17].

Generally, inorganic membranes are made from metal oxides such as Al_2O_3, ZrO_2 and TiO_2. The nature of the materials creates hydrophilic behavior due to the presences of hydroxyl groups on the membrane surface, which allows water to be greatly absorbed into the membrane pores. To prevent liquid from passing through the membrane, the membrane surface must be rendered hydrophobic for MD

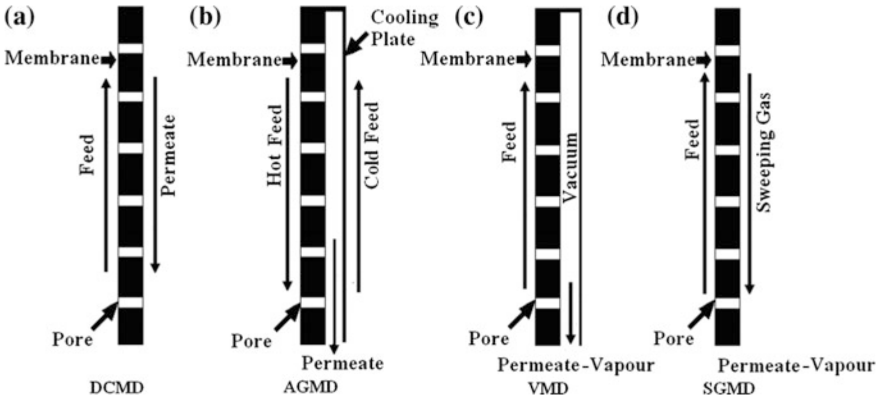


Fig. 5.3 Membrane distillation configurations: **a** direct contact membrane distillation (DCMD), **b** air gap membrane distillation (AGMD), **c** vacuum membrane distillation (VMD) and **d** sweep gas membrane distillation (SGMD) [11] (Reprinted from Camacho et al. (2013), with permission from Water)

applications, which is typically achieved by grafting of hydrophobic compounds, such as fluoroalkylsilanes [18, 19], perfluoroalkylsilanes [13, 19], and fluorodecyltriethoxysilanes [20]. Liquid entry pressure (*LEP*) is a membrane characteristic that displays the minimum applied pressure for a liquid to penetrate the pores. *LEP* depends on the maximum pore size and the membrane hydrophobicity. The value of *LEP* can be quantified by the Laplace (Cantor) equation [21]:

$$\mathrm{LEP} = \frac{-2B\gamma_L \cos\ \theta}{r_{\max}} < P_{\text{process}} - P_{\text{pore}}$$

where *LEP* is the liquid entry pressure or the minimum pressure required to pass liquid through the membrane, B is a geometric factor, γ_L is the surface tension of the solution, θ is the contact angle between the solution and the membrane surface, $r_{\max}$ is the largest pore radius, P_{process} is the liquid pressure on either side of the membrane, and P_{pore} is the air pressure in the membrane pore. For typical hydrophobic membranes, an acceptable pore size range for MD application is between 100 nm and 1 μm [10].

5.3 Membrane Geometries and Modules

5.3.1 Flat Membranes

Flat inorganic membranes are available in disc or sheet form. This geometry reduces production expenses and makes the membrane easy to examine and replace. Flat membranes are widely used in laboratory-scale applications, and the

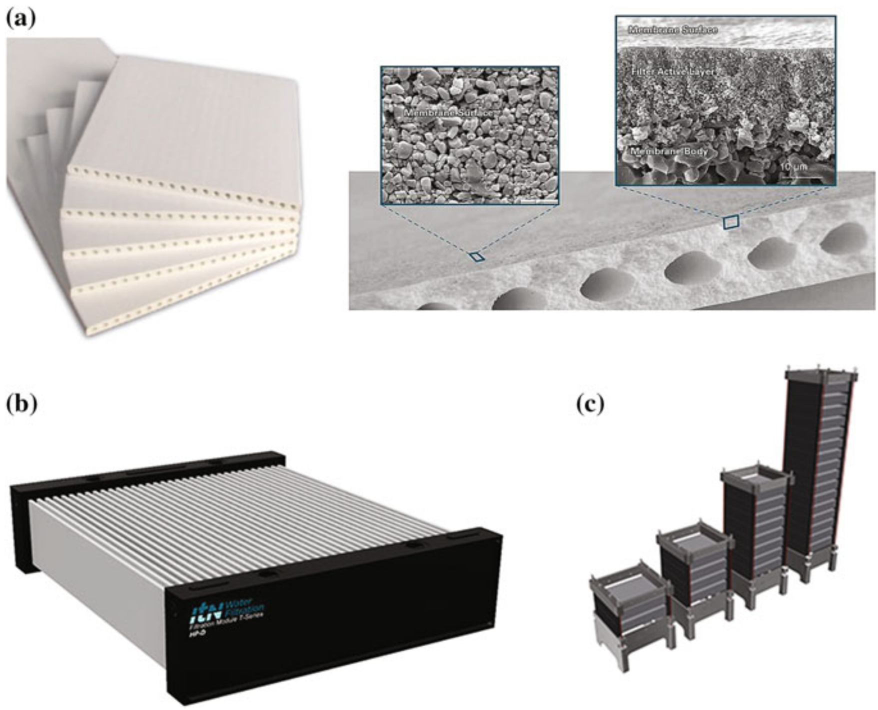


Fig. 5.4 Product photographs of **a** ItN Nanovation AG ceramic flat membrane, **b** ItN Nanovation filtration module T-Series, and **c** ItN Nanovation filtration towers [22] (Image courtesy of ItN Nanovation)

initial tests can be done with a small amount of liquid. Commercial inorganic flat membranes are available with a shape of disc with a diameter between 25 and 90 mm. For large-scale industrial and municipal applications, several single membrane plates (Fig. 5.4a) are packed in a single filtration module (Fig. 5.4b). Moreover, several modules can be further assembled into filtration towers (Fig. 5.4c).

5.3.2 Tubular Membranes

Tubular membranes can hold fluids with high concentration of oil, suspended solids, and high viscosity. They have the added advantages of permitting high flow rates along with reduced fouling. Tubular ceramic membranes can be made of one or more channels on which the membrane layers are fixed on the channel surface by some intermediate layers. Figure 5.5a shows the single- and multi-channel geometries of tubular membranes. Membrane elements are fabricated from simple tubular modules to monolithic honeycomb-type structures. Figure 5.5b shows a

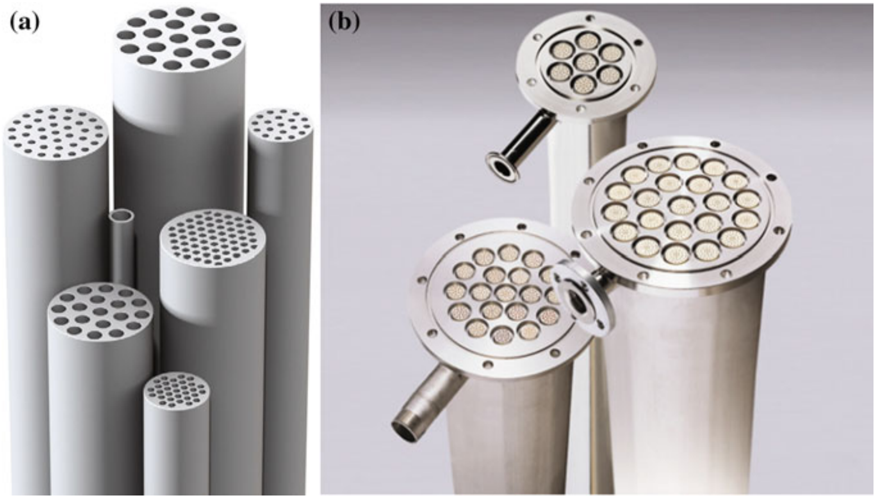


Fig. 5.5 Product photographs of **a** Schumasiv ceramic membrane filter elements of different geometries, and **b** module housings [23] (Reprinted from Heidenreich (2011), with permission from Elsevier)

housing of 7, 19, and 22 tubular ceramic membranes. Several modules are further assembled into a filtration unit for large-scale water treatment.

5.3.3 *Hollow Fiber Membranes*

Hollow fiber membrane modules have an excellent packing density and high specific surface area (Fig. 5.6). While the specific surface area of flat or tubular membrane modules is generally 100–500 m^2/m^3, the specific surface area of a hollow fiber membrane module can be as high as 4000–30,000 m^2/m^3. Therefore, hollow fiber membrane modules can be used to deal with large volumes of liquids using minimal space and energy, which is suitable for the high production demands of drinking water and wastewater treatment.

5.4 Preparation of Inorganic Membranes

Inorganic membranes are usually composites, which consist of several layers of one or more different inorganic materials. Generally, they have a macroporous support layer, intermediate layers, and a microporous top layer, as illustrated in Fig. 5.7. Preparation of inorganic ceramic membranes can be simply classified into three stages: (1) formation of particle suspension, (2) shaping of particles in the

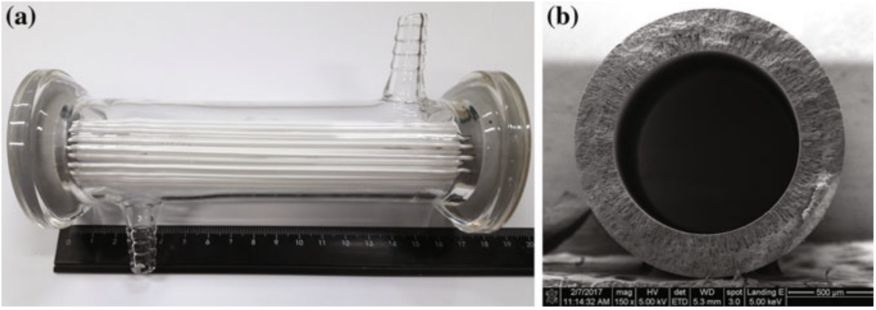


Fig. 5.6 photographs of **a** a ceramic hollow fiber membrane module, and **b** the cross-section of a hollow fiber membrane

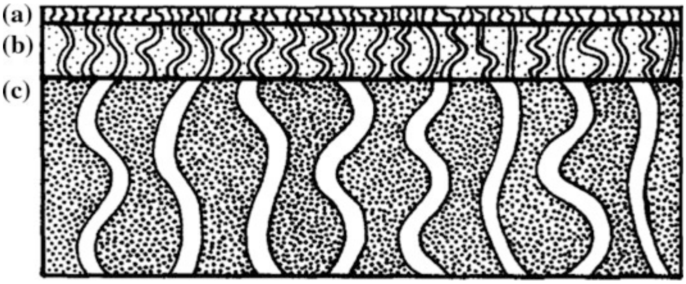


Fig. 5.7 Schematic diagram of a composite membrane: **a** top layer **b** intermediate layer and **c** porous support [25] (Reprinted from Lindqvist and Lidén (1997), with permission from Elsevier)

suspension into a membrane precursor with a desired geometry, and (3) heating of the membrane precursor [24]. After these steps, layer deposition methods are required to add layers onto a symmetric substrate to form composite membranes, tailoring the membrane selectivity as well as other membrane properties.

5.4.1 Raw Inorganic Materials

Inorganic membranes can be made from a wide variety of raw inorganic materials. Alumina, silica, titania, and zirconia are the most common materials for manufacturing inorganic membranes. However, these materials are expensive so the operating costs of inorganic membrane modules remain high for industrial applications. To reduce the membrane production costs, recent studies utilized inexpensive raw inorganic materials for the preparation of low-cost inorganic membranes, including apatite powder [26], chamotte [27], clay [28–30], quartz sand [31], kaolin [32–34], and fly ash [35–37].

5.4.2 Slip Casting

Slip casting is a simple and economical route for the preparation of inorganic tubular membranes. When a particle suspension is poured into a porous mold, the capillary action drives the solvent to diffuse through the pores of the mold. The solvent extraction causes the particles to form a cake layer on the internal surface of the mold. Then, the particle layer is consolidated rapidly to avoid particle penetration through the mold. The rate of particle deposition on the mold surface depends on the capillary pressure and the permeability of the mold. Tiller and Tsai have proposed the theory of slip casting to determine the optimum pore size of the mold [38]. The slip casting has been applied to prepare tubular MF with materials such as alumina [39, 40], zirconia [41], and fly ash [36, 37].

5.4.3 Tape Casting

Tape casting is widely used for the preparation of thin inorganic substrates with controlled thickness and good surface smoothness. During the tape casting process, the particle suspension passes beneath the knife edge as the moving carrier advances along a supporting surface. The thickness of the cast layer is determined by the gap between the knife blade and the moving carrier. For the preparation of particle suspension, inorganic powder of sufficient fineness is suspended in an organic solvent in which a binder, a plasticizer, and a dispersant are added to make the suspension homogeneous and stable. A dry membrane precursor is left on the moving carrier as the solvent is evaporated after casting [25]. The tape casting has been used to prepare alumina MF membranes [42, 43], the support for UF membranes [25], and porous metal sheets for MF [44].

5.4.4 Pressing

Pressing is commonly used to fabricate inorganic membranes for fundamental research. An applied force is used to produce the membrane using a press machine, which applies pressure higher than 100 MPa. Del Colle et al. [45] applied pressing to prepare tubular UF and MF porous and supported ceramic membranes. For the preparation of the support layer of GKN sinter metals filters, the metal powder is filled into the compacting tool made of a solid steel core and oversized outer rubber sleeve. This assembly is then sealed and immersed in a liquid inside a vessel that is then pressurized [46]. Inorganic membranes produced by pressing usually have uniform porosity and homogeneous physical properties over the total membrane part.

5.4.5 Extrusion

Extrusion is a mass productive method for producing tubular inorganic membranes. During the extrusion process, a homogeneous stiff paste is forced through a nozzle to be compacted or shaped into the membrane precursor. To keep the membrane in its desired final shape, any remaining binder, solvent, and plasticizer should be evaporated [47]. The extrusion process has been used to prepare alumina MF membranes [48] and other low-cost MF membranes using inexpensive materials such as cordierite powder [49], clay mixture, calcite and chamotte [27] and local Moroccan Perlite [50].

5.4.6 Dip Coating

Dip coating plays a key role in producing high-quality separation layers of asymmetric membranes. When a dry porous substrate is dipped into a particle suspension and subsequently withdrawn from it, the capillary suction caused by the porous substrate drives the particles to form a layer on the substrate surface. Generally, the coating thickness by dip-coating process is in the range of 100 nm–100 μm. Gu and Meng [51] have proposed a model to quantitatively describe the wet membrane formation on the substrate during the dip-coating process.

5.4.7 Sol-Gel Process

Sol-gel process is an important synthesis route for the production of inorganic membranes. This process can be divided into two main routes: the colloidal route and the polymeric route. The precursor is either a metal salt or a metal-organic compound. In the colloidal route, the precursor is mixed with water to form a colloidal sol. The colloidal sol is then coated on a membrane support, where it transforms into a gel structure consisting of a network of particles. The final membranes are mesoporous with pore sizes ranging between 2 and 10 nm, which is suitable for liquid filtration. In the polymer route, the precursor is mixed with organic solvent to form a sol, which is then coated on a membrane support, where it forms a strongly interlinked polymeric gel network. The layers produced by polymeric route are microporous with pore size less than 1 nm, which is usually applied to gas separation [24, 52]. The sol-gel method has been developed for the preparation of alumina UF membranes [53], silica membranes [54, 55], titania and alumina membranes [56, 57], titania multilayer photocatalytic membranes [58], zirconia UF membranes [59], and boehmite UF membranes [60].

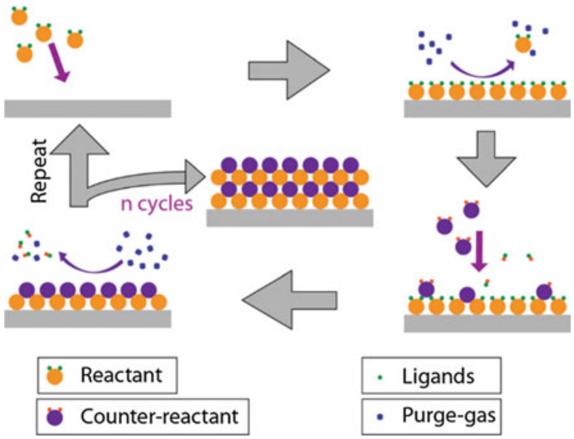


Fig. 5.8 Schematic diagram of the atomic layer deposition process [64] (Reprinted from Palmstrom et al. (2015), with permission from Royal Society of Chemistry)

5.4.8 *Atomic Layer Deposition*

Atomic layer deposition (ALD) is a self-limiting gas-phase deposition method for growing atomic scale thin films of oxides, metals, and many other materials in a wide temperature window. The self-limiting aspect of ALD leads to excellent coverage and conformal deposition on high aspect ratio structures. Therefore, ALD provides an effective method to deposit materials on porous membranes. In a typical ALD process, two precursors are pulsed sequentially and strictly separated from each other in the gas phase by a purge step (Fig. 5.8). The thickness of the deposited layer can be precisely tuned by repeating the ALD cycle [61]. Cameron et al. applied SiO_2 and TiO_2 ALD to progressively reduce the pore diameters in alumina tubular membranes. It was found that the pore diameter decreased at a rate of 1.3 ± 0.1 and 3.1 ± 0.9 Å per cycle during SiO_2 and TiO_2 ALD, respectively [62]. Li et al. tailored a ceramic MF membrane into an UF membrane using Al_2O_3 ALD [63]. The surface chemistry during ALD of common inorganic materials are described in Table 5.1.

5.4.9 *Thermal Spray*

Thermal spray is a well-established technique that requires a high temperature and high velocity flame, such as plasma jet and oxy-fuel jet to melt the feedstock materials and to deposit them onto a substrate surface. Typical mechanism for thermal spray is illustrated in Fig. 5.9. Feedstock materials are conveyed by the carrier gas, melted as they accelerate in the high temperature flame, and propelled towards a target substrate. Upon impact on the substrate, the melted particles flatten and solidify rapidly on the substrate as splats or lamellae, and the layering of splats builds uniform coatings [65]. These coatings contain myriad array of various kinds

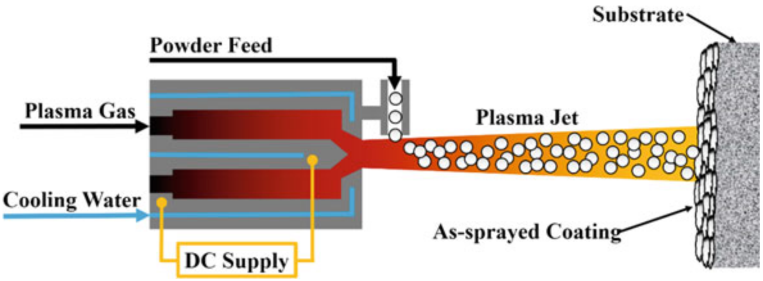


Fig. 5.9 Schematic diagram of the thermal spray process

Table 5.1 Surface chemistry during ALD of common inorganic materials [61, 62]

Materials	Surface chemistry
Al_2O_3	(A) $AlOH^* + Al(CH_3)_3 \rightarrow AlOAl(CH_3)_2^* + CH_4$ (B) $AlCH_3^* + H_2O \rightarrow AlOH^* + CH_4$
SiO_2	(A) $SiOH^* + SiCl_4 \rightarrow SiOSiCl_3^* + HCl$ (B) $SiCl^* + H2O \rightarrow SiOH^* + HCl$
TiO_2	(A) $TiOH^* + TiCl_4 \rightarrow TiOTiCl_3^* + HCl$ (B) $TiCl^* + H_2O \rightarrow TiOH^* + HCl$

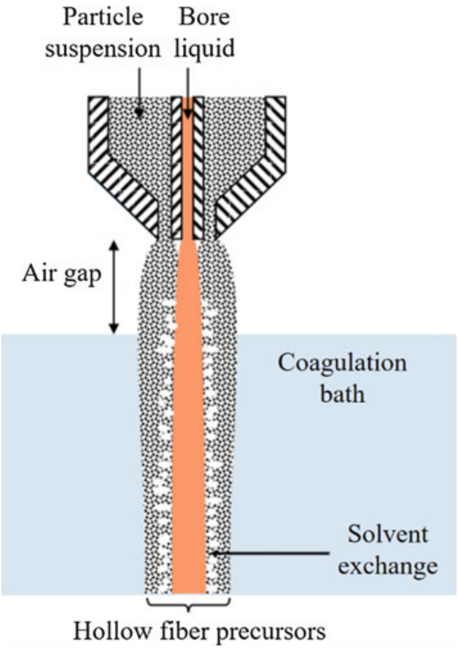
*denote the surface species

of defects, such as macro-pores, interlamellar pores and micro-pores. Thermal spray can coat almost any nonvolatile materials including metals and ceramics on various substrates. Over the past decade, thermal spray has been used to produce ceramic membranes [66, 67], cermet membranes [68] and metallic membranes [69] for water filtration.

5.4.10 *Fabrication of Inorganic Hollow Fiber Membranes*

Preparation of inorganic hollow fiber membranes can be classified into three steps: (1) preparation of particle suspension, (2) spinning of inorganic hollow fiber precursors followed by phase inversion, and (3) sintering [70–73]. Preparation of particle suspension consists of four steps in sequence: (1) mixing a dispersant and a solvent, (2) adding inorganic powder particles, (3) adding polymer binders and plasticizers, and (4) degassing. Common methods for mixing suspension are ball mixing [74, 75] and ultrasonic mixing [76, 77]. The particle size has great influences on permeability and mechanical strength. Some studies mixed powders with large and small particle sizes to enhance the mechanical strength of inorganic hollow fiber membranes. Generally, as the ratio of inorganic powders to organic binder decreases, the permeability increases and the mechanical strength of inorganic hollow fiber membranes decreases [70, 71]. Besides, suspension viscosity is

Fig. 5.10 Schematic diagrams of spinning apparatus for hollow fiber membranes [78] (Reprinted from Kim et al. (2016), with permission of Japanese Journal of Applied Physics)



also an important factor in the spinning of follow fiber precursors. In a number of studies, non-solvent (water) has been added to increase the suspension viscosity, thereby reducing the rate of phase inversion [72, 73]. Figure 5.10 shows the spinning apparatus for spinning of inorganic hollow fiber precursors. The particle suspension and the bore liquid are extruded through a spinneret using nitrogen pressure or a syringe pump to control the extrusion rate. Bore liquid and external coagulants are usually non-solvents (water). As the extruded fiber precursors entered the coagulation bath, the phase inversion occurs: the solvent from the particle suspension diffuses into the coagulation bath, whereas the non-solvent (water) diffuses into the suspension solution. During the phase inversion, the binder is not exchanged with the non-solvent in the coagulation bath. The removal of the binder takes place in the sintering step. In a spinning process, important parameters that influence the structure of hollow fiber membranes include air gap [72, 73], as well as extrusion rate of bore liquid and particle suspension.

The design of spinneret is also an important factor that influences the structure of inorganic hollow fiber membranes. In recent years, multi-channel [79, 80] spinnerets have been used to fabricate inorganic hollow fiber membranes with enhanced mechanical strength (Fig. 5.11). To figure out the criteria for spinneret designs, several studies have investigated fluid flow inside the spinnerets using computational fluid dynamics (CFD) methods [81, 82]. The structures of inorganic hollow fiber membranes can be adjusted by controlling the proportion of finger-like and sponge-like structures. The finger-like structure has larger void-channels and reduced transmembrane resistance, while the denser sponge-like structure provides

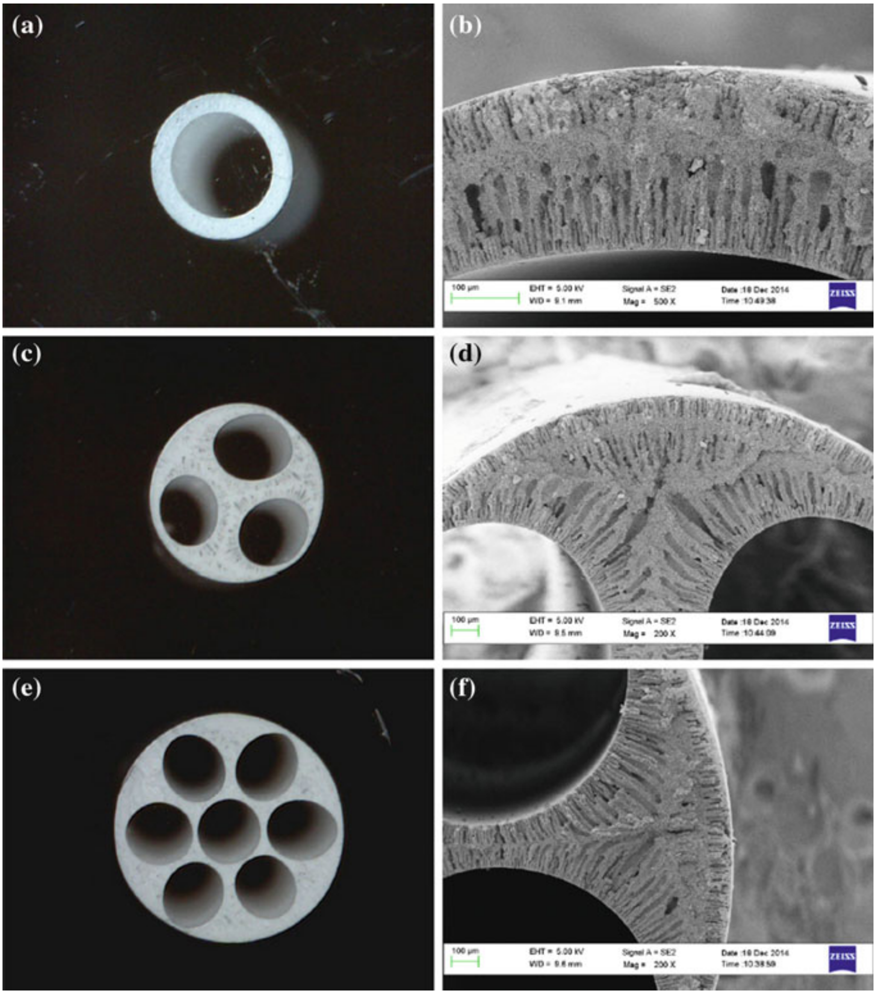


Fig. 5.11 Photographs of **a** a single-channel hollow fiber, **c** a 3-channel hollow fiber, **e** a 7-channel capillary tube, and SEM images of **b** a single-channel hollow fiber, **d** a 3-channel hollow fiber, **f** a 7-channel capillary tube [80] (Reprinted from Lee et al. (2015), with permission from Elsevier)

a better mechanical strength. Figure 5.12 illustrates the three common structures of inorganic hollow fiber with different proportions of finger-like and sponge-like structures, including symmetric [72], asymmetric [73] and sandwich structures [83]. Recent developments in X-ray computed tomography and MATLAB image analysis have provided new insights into microstructures and pore size distribution of inorganic hollow fiber membranes [84–86]. The pore size and porosity are the two important properties depending on the structures of inorganic hollow fiber membranes. These properties can further influence their separation performance and

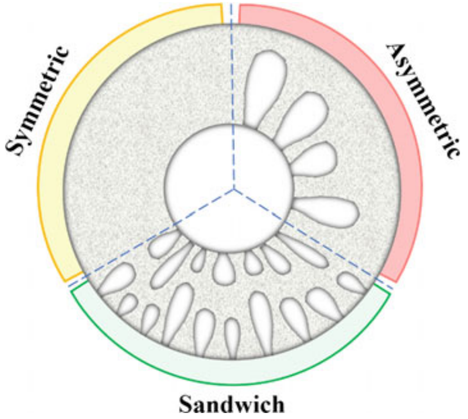


Fig. 5.12 Schematic diagram of the three structures of inorganic hollow fiber membrane

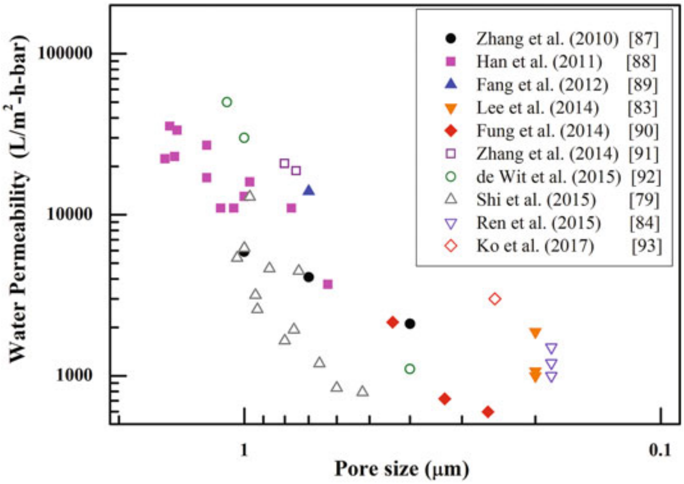


Fig. 5.13 Relationship between the permeability and the pore size of inorganic hollow fiber membranes. [79, 83, 84, 87–89, 90–92, 93]

water permeability in water applications. Figure 5.13 shows the relationship between the water permeability and the pore size of inorganic hollow fiber membranes. It is noted that a trade-off exists between the water permeability and the pore size. To optimize the separation performance, the water permeability should be increased with a fixed pore size.

5.4.11 Heating

Heating is important to determine the final properties of membranes, which consists of three stages: drying, thermolysis and sintering. Figure 5.14 illustrates the different temperatures and heating ramps of the three stages. Drying is the initial heating stage that evaporates the solvent, such as water, NMP and DMF. Common solvents have boiling points between 100 and 200 °C. Drying stage is held for 1–2 h to ensure that the solvent is removed. The second stage, thermolysis, is to remove the polymer binders and additives. Researches have been done to study the effects of temperature on the thermal decomposition of binder, and 400–800 °C is recommended for the thermolysis stage [94, 95]. The introduction of air or O_2 during thermolysis was found to facilitate the removal of organic compounds by oxidizing them into CO_2 [95]. The themolysis stage is generally held for 9–12 h to ensure the total removal of binders and additives. The last stage, sintering, allows grains to move closer to each other until they come into direct contact. The inorganic body shrinks to what will become the final membrane structure [96–99]. Sintering temperature influences the porosity and the mechanical strength of inorganic membranes. Generally, the porosity decreases and the mechanical strength increases with increasing sintering temperature. [70, 71, 100, 101] Since the ideal membrane should have both a high mechanical strength and a high porosity, the sintering temperature has to be optimized. Table 5.2 summarizes the heating processes for commonly used ceramic membranes, including aluminum oxide (Al_2O_3), yttria stabilized zirconia (YSZ), $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), silicon carbide (SiC) and silicon nitride (Si_3N_4).

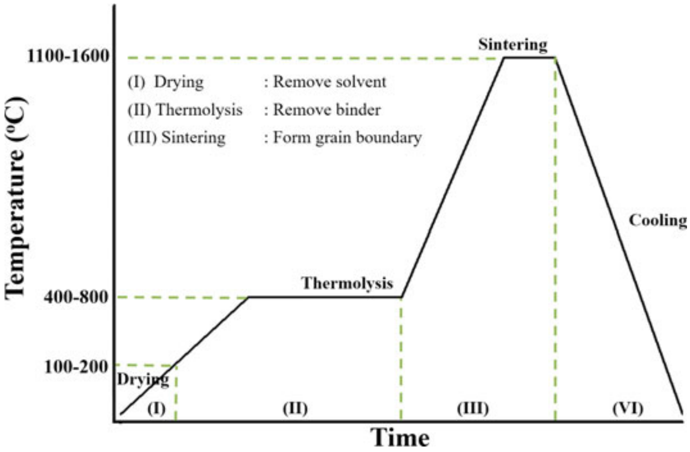


Fig. 5.14 Schematic diagram of the three stages of heating

Table 5.2 Heating procedures for common inorganic membranes

Materials	Heating procedures	References
Al_2O_3	The temperature is increased from room temperature to **400–600 °C** at a rate of **2 °C/min** and held for **2 h**, then to **1000 °C** at a rate of **5 °C/min** and held for **2 h** and finally to **1300–1500 °C** at a rate of **5 °C/min** and held for **4 h**. The temperature is then reduced to room temperature at a rate of **5 °C/min**	[72, 73, 95, 101]
	The temperature is increased from room temperature to **400–600 °C** at a rate of **2** °C/min and held for **10 h**, then to **1300–1500 °C** at a rate of **5 °C/min** and held for **2 h**. The temperature is then reduced to room temperature at a rate of **5 °C/min**	[83, 86, 102]
YSZ	The temperature is increased from room temperature to **600–800 °C** at a rate of **2–3 °C/min** and held for **2 h**, then to **1300–1500 °C** at a rate of **5 °C/min** and held for **5 h**. Finally, the temperature is then reduced to room temperature at a rate of **5 °C/min**	[87, 103, 104]
LSCF	The temperature is increased from room temperature to **1200–1450 °C** at a rate of **2–3 °C/min** and held for **4 h.** Finally, the temperature is then reduced to room temperature at a rate of **5 °C/min**	[105–107]
SiC	The temperature is increased from room temperature to **1200 °C** at a rate of **15–20 °C/min**, then to **1800–2000 °C** at a rate of **10–15 °C/min** and held for **2 h**. The temperature is then reduced to room temperature at a rate of **5 °C/min**	[108–110]
Si_3N_4	The temperature is increased from room temperature to **800–1100 °C** at a rate of **10–15 °C/min**, then to **1400 °C** at a rate of **10–15 °C/min** and held for **2–6 h**. The temperature is then reduced to room temperature at a rate of **5 °C/min**	[111, 112]
	The temperature is increased from room temperature to **1400–1450 °C** at a rate of **15 °C/min** and held for **3–8 h**, then to **1800–1900 °C** at a rate of **15 °C/min** and held for **2–4 h**. The temperature is then reduced to room temperature at a rate of **5 °C/min**	[119, 114, 115]

5.5 Commercial Inorganic Membranes

Commercial MF inorganic membranes for liquid separation were first introduced in the early 1980s, which was followed by the introduction of UF inorganic membranes in the late 1980s [116]. Today a wide variety of inorganic materials and membrane combinations are available on the market, such as SiC, Al_2O_3, ZrO_2 and TiO_2.

5.5.1 Nanostone Water Ceramic Membranes

Nanostone Water has conducted multiple pilots throughout the world with its segmented ceramic monolith (CM-151^{TM}) module (Fig. 5.15). The ceramic UF

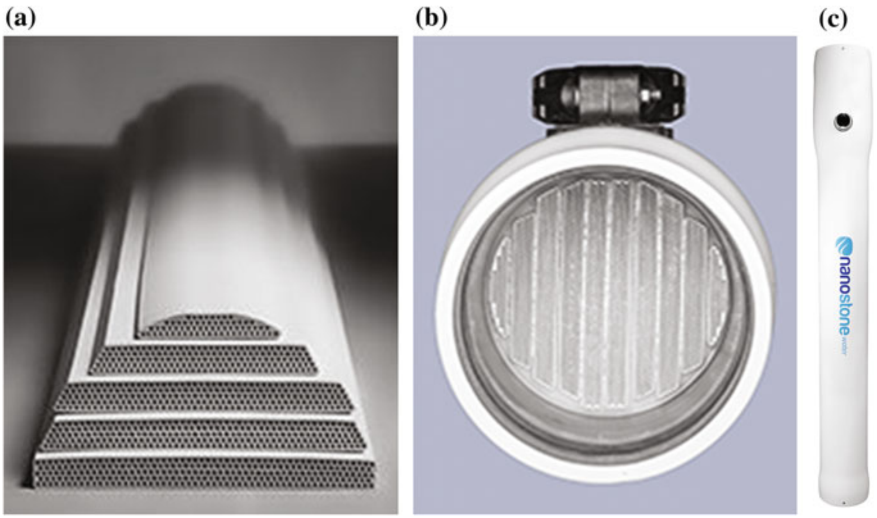


Fig. 5.15 Product photographs of **a** membrane segments, **b** potted segments and **c** a CM-151™ monolith module [117] (Image courtesy of Nanostone Water, Inc)

Table 5.3 Comparison between polymeric UF system and Nanostone ceramic UF system [117]

	Polymeric UF system	Nanostone ceramic UF system
Plant capacity	12 M L/day	
Initial capex	1.0–1.2 M USD total system	
10 year membrane Replacement cost	0.80 M USD (2 replacements)	0.00 M USD (0 replacements)
10 year operating labor cost (M USD)	0.80	0.60
10 year chemical cost (M USD)	0.45	0.45
10 year power cost (M USD)	0.14	0.17
Water recovery (M L/month discharge)	18.93 (95% recovery)	11.36 (97% recovery)
Total 10 year opex cost (M USD)	2.2	1.2
Cost of water (Capex + 10 year opex)	0.08 USD/1000 L	0.05 USD/1000 L

membranes with a high surface area are suitable to be applied in municipal and industrial water treatment. With feed water iron levels of 0.5–1.0 mg/L and turbidity ranging from 8–12 NTU, the CM-151$^{\mathrm{TM}}$ module with a nominal pore size of 30 nm can produce a stable filtration flux of 400 LMH with 98% recovery rate. In contrast, the flux is 85 LMH for most polymeric hollow fiber membranes operated under the same conditions. Based on the pilot data, the Nanostone ceramic UF system is estimated to save 1 million dollars in operating cost over 10 years compared to the polymeric UF system, and the cost of water can be reduced to 0.05 USD/1000 L (Table 5.3) [117].

5.5.2 LiqTech Silicon Carbide (SiC) Membranes

LiqTech International, Inc's SiC membranes have a very high flux up to 2000 LMH, as well as good chemical (pH 0–14) and thermal (up to 800 °C) stability. These characteristics allow the membranes to be cleaned fast with more efficient chemical cleaning, and have long life time with less maintenance, which eventually reduces the costs of the membrane systems. These robust membranes have wide applications which include oil/water separation, drinking water, wastewater treatment, and pre-RO. The SiC membrane has a monolith structure, in which a number of parallel flow channels extend through the porous membrane. The feed stream is introduced under pressure at one end of the membrane and flows through the channels during processing. The combined volume of permeate from all channels flows toward the outer shell of the membrane and is then removed continuously. Additional layers can be deposited on top of the membrane support in order to reach the desired combination of membrane pore size and water flux [118].

5.5.3 Membralox® Ceramic Membranes

Pall's Membralox® ceramic membranes feature an asymmetric membrane structure and a highly controlled surface membrane layer formed on the inner surface of a support layer. They are ideally suited for applications that involve extreme processes, such as processing feed with high solids content, the use of high temperatures, high pressures, or aggressive solvents, and where long-term stability is required. The compact multi-channel geometry and high permeability are optimized for various applications, such as UF for unwanted protein removal from antibiotic solutions, processing of alginates and other excipients, clarification of solvent extracts, and bacteria removal in high purity systems. Besides, multiple modules composed of membrane elements can be easily assembled for any scale of operation [119].

5.5.4 CeraMem® Silicon Carbide Ceramic Membranes

CeraMem® silicon carbide ceramic membranes from Veolia Water Technologies are designed for harsh operating environments unsuitable for polymeric membranes. They can be utilized in large-capacity UF and MF applications, including process streams with elevated operational temperatures, oily water, applications prone to heavy fouling, the presence of elevated solids, or pH extreme environments. About 60 commercial installations have been made and multiple pilot trials have been conducted with the present advances in the CeraMem® technology. These ceramic membrane modules are especially suitable for applications for deoiling and removing silica from oilfield produced water, as well as many other industrial applications such as industrial wastewater, chemical production, and food processing [120].

5.5.5 Inopor® Ceramic Membranes

The Inopor® membranes are available in Al_2O_3, TiO_2, ZrO_2, and SiO_2, which cover the range from MF to NF. These inorganic membranes feature a high mechanical, thermal, and chemical stability. They are stable in organic solvents, and can be operated at high permeate flux and high process temperature. The pore size of the membrane is down to 0.9 nm with a retention in aqueous solution down to 200 Da of the latest developed NF membrane. Besides, the NF selective layer can be controlled at a thickness of 50 nm, so the membrane can be operated effectively at a low pressure. The running costs can be minimized by closed production cycles and continuous processes [121].

5.5.6 InoCep® Ceramic Hollow Fiber Membranes

InoCep® ceramic hollow fiber membranes are made of stable α-Al_2O_3 material with available pore sizes ranging from 20 nm to 1.4 µm. The membranes have a long service life for highly demanding extreme processes such as the use of high temperature, pressure, or aggressive solvents as well as the processing of feeds with high solids content. Compared to multi-channel tubular membranes, InoCep® ceramic hollow fiber membranes have a higher flux, but a slower and more uniform fouling. The InoCep® ceramic hollow fiber membrane system has various applications including wastewater recycling, oily water treatment, leachate treatment, beer clarification, cold sterilization of skim milk, production of amino acid, and skim latex recovery [122].

5.5.7 GKN Sinter Metals Filters

GKN sinter metals filters are applied in many industrial gas and liquid filtration because of their high resistance to high temperature and corrosive environments. Sintered metals filters are made of stainless steels, bronze, nickel-based alloys, titanium, and several special alloys. They can be manufactured seamlessly with the length up to 1600 mm and the outer diameter of 320 mm. The membrane selective layer with filter grades down to 0.1 µm absolute has a thickness of 200 µm and is made of the same alloy as the membrane support. All sintered materials of GKN offer a self-supporting structure with high mechanical strength, so an excellent back flush performance can be achieved.

5.5.8 Metawater Ceramic Membrane Filtration System

The inorganic membrane filtration system can be used to generate clean and clear tap water by eliminating impurities and turbidity in raw water, which leads to a noticeable reduction of the chlorine demands [123]. Metawater Co. (Tokyo, Japan) has proven record in installations and maintenance of ceramic membrane drinking water plants. The company has more than 100 installations in water treatment plants. The biggest drinking water treatment plant in Kanagawa, Japan, has a daily capacity of 171,070 m^3. The Metawater ceramic membrane element is highly resistant to pressure, heat, and corrosion, resulting in no membrane breakage, which facilitates the ideal system design that meets the needs of the water treatment plants. Moreover, the ceramic membranes have a service life as long as 15 years or more. Because the membranes can be reused as a ceramic material after use, the environmental impact can be minimized.

5.6 Inorganic Membranes for Water and Wastewater Treatment

Over the past decades, inorganic membranes have been applied in a wide variety of industries thanks to their thermal stability and chemical inertness. Such advantages enable inorganic membranes to compete against traditional polymeric membranes, which are often lack of long-term stability [124]. Therefore, inorganic membranes are considered cheaper in the long run than polymeric membranes as an effective water treatment alternative.

5.6.1 Potable Water Production

Available water resources vary from surface water, underground water to municipal sewage and seawater. For the production of potable water, source water must undergo a series of purification processes including pretreatment, chemicals addition, coagulation, flocculation, filtration and disinfection to meet the criteria of drinking water. Literatures reveal that inorganic MF/UF membranes can be used to remove microorganisms, natural organic matters and groundwater contaminants. They are not easily affected by organic fouling and can be effectively cleaned to restore the permeation flux and to meet hygienic standard. Bottino et al. used microfiltration ceramic membranes for the treatment of lake water. Suspended solids were completely removed along with microorganisms and algae, and a retention of 64 and 56% was achieved for total organic carbon (TOC) and chloroform, respectively. The permeate flux was found to level off at 200 L/m^2-h as the turbidity reached a value near 80 NTU [123]. Oh et al. [125] combined ceramic microfiltration membranes and powdered activated carbon (PAC) adsorption for surface water treatment. The UV_{260} removal and dissolved organic carbon (DOC) removal were of 90.3 ± 3.2 and 80.2 ± 8.6%, respectively. Zapalis et al. used ceramic membranes in an adsorption-filtration process for water purification from arsenic As(V) ions. The arsenic content in the produced water can be lowered from 1 mg/L to 10 μg/L, with a flux of 156 kg/m^2-h under a moderate pressure difference of 3×10^5 N/m^2 [126]. Pagana et al. developed asymmetric multilayer porous γ-Al_2O_3 membranes and proposed a combined adsorption–ultrafiltration process for the removal of As(V) and Cr(III) ions from aqueous streams. Compared to the feed streams, the concentrations of As(V) and Cr(III) in the permeate streams could reduce from 1 ppm to 10 ppb and from 0.5 ppm to 10 ppb, respectively. The pure water flux was 156 kg/m^2-h under a transmembrane pressure difference of 3 bar [127]. Harman et al. investigated the effectiveness of ceramic ultrafiltration membranes with different pore sizes in removing natural organic matter (NOM) from model solutions and drinking water sources. More than 90% of UV_{280} absorbance reduction was consistently achieved in the model NOM solutions [128].

5.6.2 Desalination

Seawater and saline aquifers account for more than 97% of all water on earth; therefore, capturing even a small fraction of them can have a great impact on addressing water scarcity. While most conventional desalination technologies are energy-intensive, membrane distillation (MD) using inorganic membranes provides a more energy-efficient way for desalination. The mechanical stability of inorganic membranes allows them to be operated with stable flux, and withstand high driving force in VMD process. Table 5.4 summarizes the separation performance of various inorganic membranes in membrane distillation applications. It is noted that the flux increases with increasing temperature, and the highest flux of 60 LMH is achieved by VMD using the alumina hollow fiber membranes. Besides, the salt rejection rates recorded in the literatures are all greater than 98%, which suggests the high purity and quality of water permeate.

5.6.3 Textile Wastewater Treatment

In textile dyeing industry, the discharge liquids include caustic alkaline solution of sodium hydroxide, reactive dyes, aromatic compounds, and surfactants. [140]. MF

Table 5.4 Separation performance of inorganic membranes in membrane distillation

Types	Materials	Geometries	NaCl feed	Feed temperature	Flux (L/m^2-h)	Ref
DCMD	Al_2O_3/ZrO_2	Tubular	1.0 M	60 °C (95 °C)	1.1 (6.9)	[12]
DCMD	Al_2O_3	Flat	0.1 M	53 °C	9.0	[13]
VMD	Al_2O_3	HF	4.0 wt%	60 °C (70 °C) [80 °C]	19.0 (32.0) [42.9]	[19]
AGMD	Al_2O_3/ZrO_2	Tubular	1.0 M	75 °C (85 °C) [95 °C]	1.7 (2.9) [5.0]	[20]
DCMD	Al_2O_3	Flat	4.0 wt%	60 °C (70 °C) [80 °C]	7.1 (11.5) [17.0]	[84]
VMD	Si_3N_4	HF	4.0 wt%	60 °C (70 °C) [80 °C]	14.6 (22.9) [27.5]	[91]
DCMD	Si_3N_4	HF	4.0 wt%	60 °C (70 °C) [80 °C]	5.4 (7.5) [10.4]	[91]
DCMD	ZrO_2/TiO_2	Tubular	0.5 M	75 °C (85 °C) [95 °C]	1.7 (2.5) [3.8]	[129]
VMD	ZrO_2/TiO_2	Tubular	0.5 M	40 °C	7.5	[129]
AGMD	ZrO_2/TiO_2	Tubular	0.5 M	75 °C (85 °C) [95 °C]	2.7 (3.3) [4.7]	[129]
AGMD	ZrO_2/Al_2O_3	Tubular	1.0 M	65 °C (80 °C) [95 °C]	1.0 (2.9) [6.9]	[130]
VMD	Si_3N_4	HF	4.0 wt%	50 °C (60 °C) [70 °C]	9.6 (14.6) [22.2]	[131]
AGMD	ZrO_2	Tubular	0.9 wt%	50 °C (60 °C) [70 °C]	2.3 (3.9) [7.0]	[132]
AGMD	TiO_2	Tubular	0.8 M	70 °C (80 °C) [90 °C]	0.8 (1.5) [2.8]	[133]
DCMD	TiO_2	Tubular	0.8 M	70 °C (80 °C) [90 °C]	0.6 (1.0) [2.5]	[133]
VMD	Zeolite/Al_2O_3	Tubular	3.5 wt%	60 °C	12.0	[134]
VMD	Al_2O_3	Flat	4.0 wt%	60 °C (70 °C) [80 °C]	5.8 (7.9) [10.4]	[135]
DCMD	β-Sialon	HF	4.0 wt%	60 °C (70 °C) [80 °C]	3.8 (5.4) [6.7]	[135]
SGMD	Al_2O_3	Flat	4.0 wt%	70 °C (80 °C) [90 °C]	9.9 (13.1) [19.8]	[136]
SGMD	Si_3N_4	Flat	4.0 wt%	75 °C	6.7	[137]
VMD	Al_2O_3	Flat	3.5 wt%	70 °C	37.1	[138]
VMD	Al_2O_3	HF	3.5 wt%	70 °C	60.0	[139]

is well suited for removing colloidal dyes and flocculation of cotton or fabric. In membrane treatment of secondary textile wastewater, MF serves as a pretreatment ahead of UF or NF. Rozzi et al. reported an inorganic membrane-based MF, which was made of ZrO_2 supported on an Al_2O_3–TiO_2 monolite. The residual pollutants of MF effluent could be subdivided into two fractions including 300,000 and 3000 Da with 45–50% COD [141]. Tubular titanium dioxide fused ceramic membranes were documented for the removal of sodium nitrate and dyes. Dyes rejection could be up to 99% under suitable conditions, while salts rejection ranged from 12 to 64% [142]. UF was reported as a single-step treatment of secondary textile wastewater, and the quality of permeate was only allowed for reuse in the minor processes such as rinsing and washing [143]. For wastewater reuse or chemical reclamation, NF is employed to further purify the MF permeate. Chen et al. compared a ceramic NF membrane with two commercial spiral-wound organic NF membranes. The results showed that the ceramic NF membrane had high dye rejection and medium salt rejection [144]. The permeate of the NF membrane could be treated with a membrane crystallizer to retain salts in the solution. From the perspective of circular economy, the recycled water can be redirected to front-end processes and these salts or chemicals can also be reused for previous processes.

5.6.4 Oily Wastewater Treatment

The inorganic membranes have been widely applied in oily wastewater treatment because of their potential traits, such as hydrophilic properties, mechanical, and chemical stabilities. Yang et al. synthesized ZrO_2/α-alumina MF membranes for oil water separation. The membranes had a pore size of 0.2 μm, with an oil rejection of 99.8% and permeability of 93 L/m^2-h-bar [145]. Mohammadi et al. prepared kaolin MF membrane with a pore diameter of 10 μm to treat oil in water emulsions. The prepared membranes provided a good separation performance for oily wastewaters with concentration lower than 2000 ppm [146]. Cui et al. fabricated NaA/α-Al_2O_3 MF membranes for oily wastewater treatment, and an oil rejection of 99% was obtained with a flux of 85 LMH at a membrane pressure of 50 kPa. The membrane performance could be maintained by frequent backwash with hot water and alkali solution [147]. Kumar et al. prepared low-cost tubular ceramic MF membranes using an extrusion technique with inexpensive clay mixtures. The prepared membranes had an average pore size of 0.309 μm and mechanical strength of 12 MPa. The oil rejection of 99.98% was attained at an applied pressure of 69 kPa [30].

5.6.5 Wastewater Treatment for Electronics Industry

Electronics industry has rapidly grown since the late twentieth century. This industry creates huge production value but inevitably generates a large amount of wastewater. Tetramethyl ammonium hydroxide (TMAH) is a toxic organic alkali widely used in semiconductor manufacturing processes. The TMAH wastewater should be treated carefully or it may pose a threat to health and burden the environmental load. Nishihama et al. prepared an MFI-type zeolite-coated membrane for NF of TMAH The results showed that the TMAH was not detected in the permeate when the operating pressure was at 0.08 MPa. The MFI-type zeolite-coated membrane could be repeatedly used for NF by backwashing the membrane with dilute hydrofluoric acid between cycles [148].

5.6.6 *Juice Clarification and Concentration*

Inorganic membranes have been successfully applied for juice clarification by safely removing suspended solids in juice filtration applications, and providing exceptional clarity without stripping color. Jegatheesan et al. applied micro- and UF ceramic membranes to clarify limed and partially treated sugarcane juice. The recovery of the membranes after a filtration cycle could be carried out effectively through chemical cleaning [149]. Wang et al. used tubular ceramic MF membrane to clarify West Indian cherry juice. The chemical composition of the permeate was sterile and closely approximated to the original one [150]. Nandi et al. prepared low-cost ceramic MF membranes for the clarification of mosambi and orange juices. After MF, important properties like TSS, pH, acidity, and density of the juice were almost unaffected, while the significant improvement in juice color, clarity, and alcohol insoluble solid was observed [151, 152]. Gomes et al. evaluated the effect of MF on the lycopene content and antioxidant capacity of watermelon juice using ceramic membranes with an average pore size of 0.1 μm. For the most concentrated extract, the lycopene concentration and antioxidant capacity were enhanced by 402.8% and 416.3%, respectively [153]. For the juice concentration, Hirota et al. prepared hydrophobic Al_2O_3 membrane by grafting $C_6F_{13}C_2H_4Si(OC_2H_5)_3$ and applied the membrane to a VMD system for concentration of sucrose solution. By exposing the membrane to a sucrose solution of 10 wt% at 60 °C, a water flux could attain 7.2 kg/m^2-h [154].

5.7 Conclusions

Applications of inorganic membranes in water and wastewater treatment have received considerable attention because of their well-recognized advantages compared to polymeric counterparts. Inorganic membranes can withstand harsh environments in wastewater treatment and aggressive cleaning methods. The applications of inorganic membranes can not only reduce membrane cleaning and replacement, but also increase process efficiency. However, the production costs of inorganic membranes are still high, so novel methods have to be developed to prepare inorganic membranes at lower cost. The viability of inorganic membranes hinges on the developments of inexpensive raw materials and scalable processing methods. To offer great treatment capacities for large-scale applications, inorganic hollow fiber membrane modules with excellent packing density can provide a higher flux compared to other inorganic membranes with different geometric membrane designs. The competitiveness of inorganic membranes has been demonstrated in many water treatment applications, and more than 100 water treatment plants have been installed by Metawater Co. (Tokyo, Japan). As sustainability has become increasingly important, inorganic membranes are a promising candidate to treat water and wastewater more efficiently, and in the long run save money and conserve water.

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Chapter 6
Desalination by Reverse Osmosis

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Abstract This chapter deals with the main techno-economic and environmental issues involved in assessing the sustainability of RO membrane technology for water desalination. The technical and economic aspects of desalination plant design and operation are reviewed, focusing on the key parameters of specific energy consumption (SEC) and product water unit cost, which are significantly affected by the main RO process part of the plant. Analysis of factors affecting these parameters helps to identify technical areas for improvements, particularly for seawater desalination. Improving the efficiency of high pressure pumps and of energy recovery devices as well as the permeability and antifouling characteristics of RO membranes appear to be high priority R&D targets, combined with efforts to improve membrane module design. Regarding environmental impact, in addition to SEC, the raw water intake facility and the effluent-brine handling practices tend to get increasing attention and are expected to dominate in the overall sustainability assessment in the coming years, despite their modest direct contribution to the product water unit cost at present. Consequently, there is also a clear priority for R&D work related to the intake facility and the brine handling and/or utilization methods. Difficulties encountered in implementing a comprehensive sustainability assessment of RO membrane desalination are outlined.

Keywords RO desalination · Sustainability assessment · Techno-economic and environmental issues · Specific energy consumption · Product water unit cost · Feedwater intake and pretreatment · Concentrate handling · R&D priorities

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List of Symbols

b	Leakage ratio of ERD
C_W	Salt concentration at the membrane surface
(C_{Wi})	Local salt concentration at membrane surface element ΔA
C_b	Salt concentration in the retentate bulk
J_i	Local flux at membrane surface element ΔA
P_f	Feed pressure
P_b	Concentrate pressure
P_o	Permeate pressure
P_{Ri}	Local retentate-side pressure
P_{Pi}	Local permeate-side pressure
Q_b	Brine flow rate
Q_f	Feed flow rate
Q_l	Leakage flow rate in ERD
Q_P	Total permeate flow rate
Q_{Pi}	Local membrane permeation flow rate ($=J_i\ \Delta A$)
Q_{Ri}	Local retentate flow rate
q_{Pi}	Local flow rate in the permeate channel
R	Desalinated water recovery
R_m	Clean membrane resistance
R_c	Membrane fouling resistance
SEC	Specific energy consumption
SEC_i	SEC under ideal conditions, i.e., zero inefficiency of pumps and ERD
$\mathrm{SEC}_{\mathrm{inef}}$	SEC due to nonideal pump and ERD operation
$\mathrm{SEC}_{\mathrm{OS}}$	SEC to overcome osmotic pressure
SEC_f	SEC due to membrane filtration resistance
SEC_R	SEC due to fluid friction losses in the SWM module retentate channels
SEC_P	SEC due to fluid friction losses in the SWM module permeate channels
$\mathrm{SEC}_{\mathrm{min}}$	SEC to overcome the osmotic pressure of the bulk fluid
$\mathrm{SEC}_{\mathrm{CP}}$	SEC due to concentration polarization
W_{total}	Total hydraulic power
$\Delta\pi(C_W)$	Osmotic pressure difference across the membrane
ΔP	Pressure difference across pressure vessel
ΔA	Membrane surface element for local computations
ΔP_{Ri}	Local pressure difference at the retentate channel
ΔP_{Pi}	Local pressure difference at the permeate channel
η_E	Pressure transfer efficiency of ERD
η	Overall pump efficiency
η_{hydr}	Hydraulic pump efficiency
η_{motor}	Electrical motor efficiency
η_{VFD}	Variable frequency drive efficiency
μ	Water viscosity

6.1 Introduction

6.1.1 Current Status and Trends

Desalinated water has evolved into a viable alternative potable water supply, mainly in the past two decades, due to increasing water scarcity worldwide. Although desalination provides at present only around one percent of the world drinking water, this percentage is growing at a high rate [1]. Specifically, at the end of 2015, approximately 18,000 desalination plants were operating worldwide, with a total installed production capacity ~87 million m^3/day. Approximately 44% of this capacity (37.32 million m^3/day) was located in the Middle East and North Africa. Moreover, during the next decade, desalination in that region is projected to grow annually at a rate of 7–9%, whereas several other "hot spots" for accelerated desalination development exist in Asia (notably in China), the US and Latin America. According to a recent comprehensive report [2], corroborating these predictions, the global market for public–private partnership (PPP) projects in the water sector, is estimated to almost triple between years 2016 and 2020, by addition of an average 16 million m^3/day of water treatment capacity annually, versus approximately 6 million m^3/day between 2010 and 2015. To achieve this growth, the total investment during the 2016–2020 period is expected to exceed US$58 billion, of which 80% will target new seawater desalination and wastewater treatment plants [2]. *Specifically for water desalination, the planned capacity increase during the 2016–2020 period is estimated to be 8.5 million* m^3*/day, i.e., ~10% of the current total global desalination capacity*. The great majority of that capacity will be covered by RO membrane desalination. The review of historical data on the technical and economic aspects of desalination summarized by Ghaffour et al. [3] confirms these trends, showing that over the last two decades, the installed capacity of RO membrane desalination has increased from the level of 10 million m^3/day in 1995 to its present level exceeding 60 million m^3/day. This trend of sharp increase of water desalination (largely by RO membranes) is expected to continue in coming decades, due to increase of world population, changing climate patterns as well as limited availability of new and inexpensive freshwater supplies.

Considering source waters, currently desalinated water is produced either by desalting brackish water (with salt content less than 10,000 mg/L), or seawater with salinity in the range ~30,000 to ~45,000 mg/L [4]. Although desalination of brackish water is less energy consuming, leading to reduced cost of product water, it is questionable whether it can be a main source of alternative feedwater in the future. Indeed, the total volume of brackish water worldwide is limited (to less than 1% of the global water availability) and in most arid regions of the world it is almost fully utilized [1]. Inevitably seawater, currently comprising over 97% of the earth water resources, will be the main source for membrane desalination. However, another kind of low-salinity feedwater, to be reckoned with in the near future, will be the various types of treated effluents, which are largely discharged to the environment at present.

Regarding RO membrane desalination economics, significant reduction of product water *total unit cost* has taken place in the past two decades, from over 2$/m^3 to the present level (for fairly large plants) of ~0.5–1$/m^3, depending on local conditions and available energy sources (e.g., [3, 5]). This cost reduction is the result of significant technological improvements, including membranes of increased permeability and salt rejection [6–9], high pressure pumps and energy recovery devices (ERD) of improved efficiency [10–12] improvements in membrane module design as well as in overall system design and operation. [9, 13, 14]. Additionally, these improvements have led to substantial reduction of capital expenses, which, at present, are significantly less than 1000$ per unit capacity (m^3/day), for RO plants of capacity greater than 100,000 m^3/day [3, 9, 13]. In parallel, the confidence gained through the successful operation of large capacity plants [15, 16] has led to the establishment of the RO membrane process as the undisputed leader in the desalination field, at present and for the foreseeable future [4], despite progress made toward the development of alternative technologies, such as Membrane Distillation (MD) [17], Capacitive Deionization (CDI) [18], Electrodialysis (ED) [19], etc.

The above positive trends at the technological side have reduced the risk for investing in RO plants [2], and (combined with the presently reduced price of fossil fuels) have encouraged investors and decision-makers, thus prompting the planning and construction of even larger RO-based desalination plants, especially those already operating around the Mediterranean and in the Middle East; e.g., in Algeria (Magtaa RO plant producing 500,000 m^3/day potable water) and in Israel, where the Sorek plant with capacity 624,000 m^3/day is the largest worldwide [20].

These very large plants, obviously can achieve reduced total product water cost due to economies of scale. However, setting aside clear benefits, related to the secured and steady potable water availability, afforded by the ever increasing number of RO plants, other possible significant impacts of their construction and operation have to be considered.

6.1.2 Sustainability Issues of RO Desalination

The very rapid growth of RO membrane desalination for potable water production raises justifiable concerns regarding its *sustainability*. In recent years, it has been recognized [21] that sustainability, especially of major endeavors involving natural resources, should be assessed by addressing three classes of issues, i.e., *economic, environmental* and *social*. These classes are alternatively termed *sustainability pillars*. In a very recent study, a comprehensive critical review of the state of the art regarding sustainability analysis related to desalination has been provided [22]; moreover, a methodology for quantitatively assessing sustainability has been proposed, aiming to account (through a unified framework) for economic, environmental, and social issues in an integrated manner. The main target of this method is the determination of a *composite sustainability index* (CSI) as a function of relevant parameters/metrics that quantify all the aforementioned key issues related to a project, which would allow (among other possible outcomes) sensitivity analyses and a kind of overall optimization of project design, implementation, and operation. This method is considered a step in the right direction, despite the fact that, at this early stage of its development, reliable application is an extremely difficult (almost impossible) task, mainly due to the need to quantify a fairly large and assorted number of parameters (representing dissimilar issues) and to recast them in the form of manageable sustainability indices. Lior [22] provides a rather thorough coverage of the sustainability issues and a related extensive literature survey, including other approaches currently taken; the following brief outline is made for the sake of completeness of this chapter.

The sustainability analysis of a desalination project should be placed in an adequately broad spatial and temporal perspective. Regarding the latter, all activities and aspects related to project should be considered; i.e., planning, design, construction, plant commissioning, operation and even decommissioning. Spatially, an analysis should account for possible effects extending beyond the plant vicinity, as is the case of released "greenhouse gases" related with the energy consumption, and the disposal of plant effluents.

The economic issues to be considered in a sustainability assessment should comprise the *total cost* of the desalinated water, in an all-inclusive manner. In addition to common costing practices, including O&M expenses, direct and indirect capital costs, other issues should be accounted for; e.g., the impacts of produced water on the local and national economies, alternative ways for supplying the needed water, reduction of water demand through more efficient use, including water pricing policy that would lead to efficient resource utilization. In this chapter, regarding economic issues, it is considered sufficient to assess and provide information on the itemized contributions of the various sections of a desalination plant on the capital costs as well as on the unit cost of product water.

The environmental issues should comprise all the effects related to abstraction of the feedwater and the disposal of desalination process liquid and solid wastes to the environment, as well as the emissions due to the energy consumption in the entire RO plant. Additionally, one should consider the long-term impact on the existing freshwater resources and on the various water consuming sectors (including agriculture and industry) within a defined geographic domain. The environmental issues are complicated, as the large quantities of feedwater and effluents of the new RO plants might affect the local ecosystem. Fairly comprehensive discussion of environmental issues related to desalination is available in the literature (e.g., [23–25]). In this chapter, the major issue of specific energy consumption (SEC) per unit volume of desalinated water is dealt with in fair detail; additionally, a review is provided of the current status of dealing with the seawater fed to a desalination plant and the disposable concentrate and related compounds.

The social issues involve impacts on human health, employment, and other likely effects on the quality of life and of social concern due to desalination facilities (e.g., impact on local infrastructure, recreational land and resources). These social issues are considered beyond the scope of this chapter and are addressed only in general terms through the description of the various sections of the desalination plant and the related economic and environmental aspects.

The analysis of economic and environmental issues of the RO plants design/construction and operation, made in the following sections, will help identifying particular factors at the technical level that would facilitate implementation of sustainability assessment.

6.1.3 Scope

This chapter deals with the aforementioned key techno-economic and environmental issues, regarding the sustainable application of RO membrane technology for water purification, focusing on saline water treatment for potable water production. Considering the state of the art of RO membrane technology, particular objectives include:

(a) Review of the technological aspects of RO desalination that underline the environmental and economic pillars of a comprehensive sustainability assessment.
(b) Assessment of the key issues by considering the main factors, particular processes and practices involved in a typical project that could be improved or optimized, thus enhancing the sustainability of RO membrane desalination.
(c) Prioritization of R&D areas regarding RO plants from the standpoint of sustainability.

To facilitate presentation, without losing generality, this chapter will focus on medium and large-scale RO water desalination plants, for treatment of *seawater* (SW) and *brackish water* (BW).

6.2 The RO Desalination Plant

6.2.1 General Plant Layout

A typical RO membrane desalination plant for potable water production is comprised of the following main sections (Fig. 6.1): (1) *the feedwater intake facility*, (2) *the pretreatment section* to improve the quality of the feedwater to the main desalination plant, (3) *the main RO desalination process section*, where high-quality water is produced, (4) *the posttreatment section,* where the product water composition is commonly adjusted for human consumption and (5) *the disposal/treatment facility mainly* handling the concentrate from the RO process. The type of available raw water to be treated, in particular the organic and inorganic load, determines to a large extent the plant complexity and the design of the

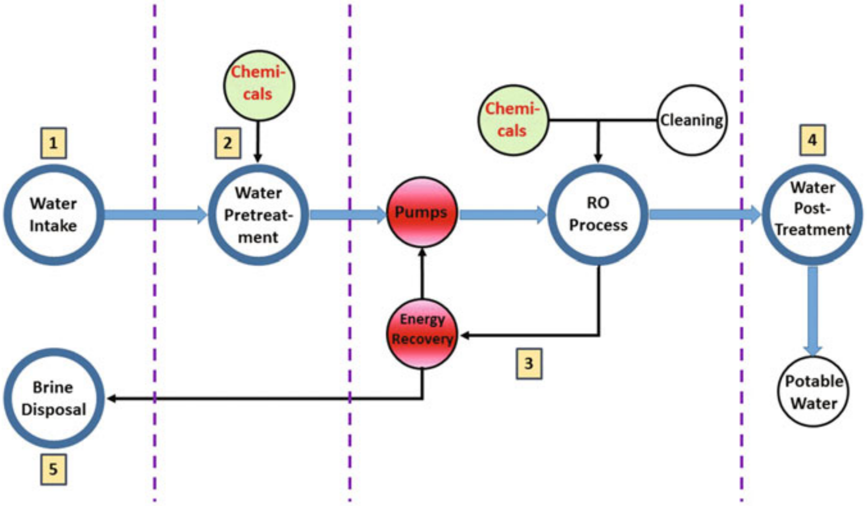

Fig. 6.1 Schematic layout of a typical RO membrane desalination plant for potable water production

aforementioned sections. For instance, in the case of relatively clean raw water from subterranean wells of fairly stable productivity, the pretreatment section is relatively simple, with no particular technological issues. On the contrary, saline surface waters or seawater, normally characterized by significant organic load (among other pollutants), require a well-designed pretreatment section, whereas the function of seawater intake facility is a major concern in all phases of the desalination project. Similar arguments hold regarding the brine treatment and/or disposal facility. The general layout, schematically shown in Fig. 6.1, is typical of a seawater desalination plant and will be employed for the purposes of this presentation; differences of this layout, mainly due to particular raw water quality and local conditions, will be also discussed.

6.2.2 Feedwater Intake Facility

This section is of particular significance in the case of seawater desalination. Natural seawater contains a variety of organic and inorganic matter which is detrimental to the RO treatment process [26]. The variety of organic and inorganic matter present in the seawater, listed in Table 6.1 [27], is indicative of colloidal and other species that should be removed from the raw water (to the greatest practical extent) before it is fed to the RO membrane desalination process. Additionally, depending on geographic location, open-ocean intakes may be subject to seasonal clogging by seaweed [28] and/or jellyfish. Other periodic natural events in some areas, such as harmful algal blooms and red tides, can overwhelm the pretreatment

Table 6.1 Colloidal and other matter in natural waters [27]

Microorganisms
Biological debris (plant and animal)
Polysaccharides (gums, slime, plankton, fibrils)
Lipoproteins (secretions)
Clay (hydrous aluminum and iron silicates)
Silt
Oils
Kerogen (aged polysaccharides, marine snow)
Humic acid/lignins/tannins
Iron and manganese oxides
Calcium carbonate
Sulfur and sulfides

facilities and cause shutdowns of RO plants [29, 30]. In view of these possible adverse conditions, not uncommon in many parts of the world, three main targets are usually set regarding the selection and design of an appropriate raw water intake system: (a) *Stability of operation and steady feedwater rate* throughout the year. (b) "*Fair" quality of raw water*; i.e., feed stream with reduced (as much as possible) organic, colloidal, and other dispersed matter that would in turn reduce the load of following pretreatment facility. (c) *Minimization of the environmental impact* due to the steady abstraction of large quantities of seawater.

It is evident that the feedwater quality provided by the intake facility is intimately related with the pretreatment system. "Fair" quality of the raw water can lead to reduction in the complexity of pretreatment system, thereby both reducing the need for physical-chemical treatment and the amount of additives, and increasing the operational reliability of facilities. Under such conditions of feeding fair quality raw water into the plant, the capital expenses for construction of pretreatment processes as well as the related operating costs are reduced. Therefore, this issue of "fair" quality of raw water provided by the intake facility, over the entire useful life of the desalination plant, in connection with the potential environmental impact of abstracting large quantities of seawater from a certain (commonly coastal) area, has a direct impact on the life cycle cost of desalinated water and on the sustainability of the entire desalination project.

The two main types of intake systems used for seawater RO desalination plants are *beach wells* (or *subsurface intakes*) and *open-surface intakes* [16, 31, 32]. Open intakes are placed above the seafloor and are a common type of intake system for medium and large desalination plants [31]. Subsurface intakes comprise buried pipes and/or wells drilled at the shore or in the sea/ocean floor [32], whereas the seawater is drawn through the subsurface formation into the intake pipe. The subsurface geological conditions usually pose limitations to the capacity and performance of the subsurface system as compared to open intakes. However, feedwater extracted through beach well intakes is usually of better quality (compared to that from open intakes) regarding the presence of undesirable matter such as assorted colloids, oil and grease, natural organic contaminants and aquatic microorganisms. To date, wells are apparently the most common types of installed intake systems especially for relatively small-capacity plants, according to data presented by Missimer et al. [32], although it is considered [33] that this trend may change as the number of seawater desalination plants grows, in diverse locations. In the case of brackish water desalination, the sources of feedwater to RO plant are commonly either surface water sources or subsurface wells, the latter also of better quality due to the natural filtration of the subsurface soil formations.

Possible environmental impacts associated with conventional seawater open intakes, mainly include *impingement and entrainment* of marine biota, which can also create large permitting costs and construction delays [23, 34]. There are also direct and indirect environmental impacts associated with the use of chemicals, to keep clean the intake piping system, as well as coagulants and additives required in the pretreatment processes [35]. On the other hand, seawater intake *wells*, if feasible, are reported [33] to be economical for desalination plants with relatively small production capacities (i.e., less than 10 mgd or 38,000 m^3/day) and tend to be favored in some countries (such as the United States) by regulatory agencies mainly due to their reduced environmental impact.

The issues involved in assessing the intake systems are discussed in several publications [16, 23, 31–34]. In view of the importance accorded to intake facility type and function, the selection of an appropriate technology tends to be fairly complicated, requiring a significant amount of information of various types. Therefore, considered from the overall sustainability assessment standpoint, the choice between subsurface intakes and open-surface intakes should be settled only on a case-by-case basis, although there are strong and well-documented arguments (e.g., [32]) in favor of the subsurface intakes. Mackey et al. [33] in a fairly comprehensive report analyze the issues involved in assessing seawater intake systems for desalination plants. Considered from a broad perspective, the selection of an appropriate technology at the project planning stage requires a variety of information from several sources to address the following types of issues: *Site conditions, Technology options, Permitting requirements, Environmental impacts, Stakeholder values and Utility constraints and interests.* These authors have also developed a decision-making tool regarding intake system selection that is useful in the planning stage of a desalination project.

Additional information on the capital and operating cost as well as the sustainability assessment of the intake facilities is provided in subsequent sections.

6.2.3 Pretreatment Section

The pretreatment facility design and operation depends on the raw feedwater quality, which, in turn, is essentially determined by the type of intake system employed, as outlined in the foregoing section. The performance of the pretreatment facility is critical for the good overall performance of the desalination plant, i.e., the fouling free (as much as possible) operation of the RO process, in particular in the case of seawater. Complicated and costly pretreatment processes are commonly required in order to control biofouling, colloidal and organic fouling of the RO spiral-wound membrane (SWM) modules [36], in the case of raw water obtained through an open intake facility. However, the pretreatment process required in the case of raw water from a subsurface intake, is generally much simpler and inexpensive. Figure 6.2 presents schematically [32] typical block diagrams of several pretreatment process trains for the aforementioned two types of intake facilities. In general, the pretreatment facility for raw water from sub-surface intake is relatively simple with rather limited uncertainty regarding both performance and cost estimation at the design stage [16, 32]; nonetheless, concerns usually exist for the possible occurrence of biofouling due to the ever-present microorganisms despite the generally clean feedwater and the good function of filters. However, the type of pretreatment of raw water from *open intakes* is a matter still rather extensively researched [36] with several key issues still unsettled [24]. The dominant issue is the optimal configuration or combination of particular operations; i.e., chlorination, screening, coagulation combined with either flocculation/settling or dissolved air flotation (DAF), dual-media filtration, ultra- or microfiltration [24, 37, 38]. Before the turn of the twentieth century, seawater pretreatment was dominated by conventional processes and in particular by dual-media filtration. It is argued [36] that the tremendous growth of RO membrane desalination in the past 20 years is correlated with introduction of membrane operations for effective pretreatment. Membrane-based pretreatment for SWRO is

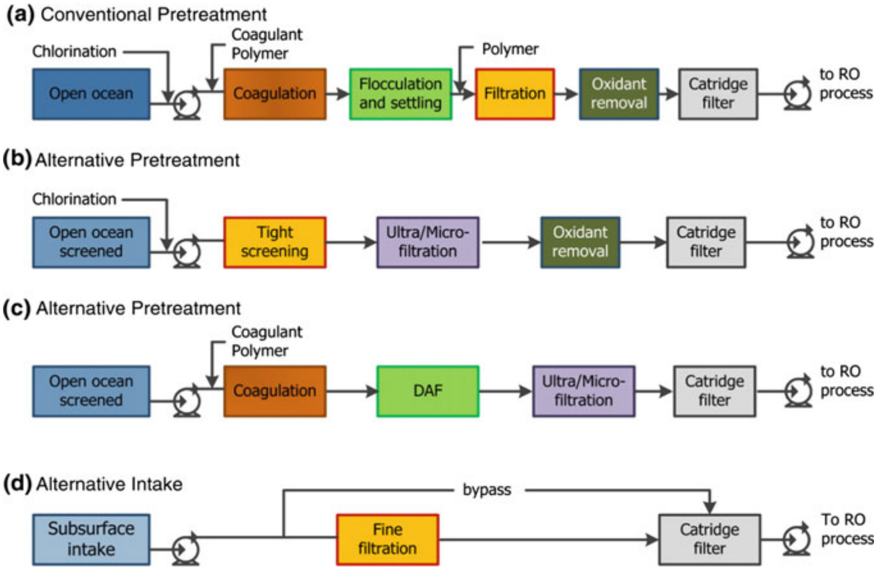

Fig. 6.2 Typical pretreatment process trains for a SWRO plant [32]. **a**–**c** Alternatives to treat seawater from an *open intake*; **d** a targeted simplified system to treat seawater from *subsurface intake*. Reprinted with permission from Ref. [32]. Copyright © 2013 Elsevier

considered expensive [16], mainly due to the increased capital expenditure. However, membrane processes (in particular those employing UF membranes) exhibit distinct advantages over conventional methods regarding disinfection, organic matter rejection, and overall sustainable performance [37, 39, 40]. Regarding sustainability, a life cycle cost assessment [41] based on 2006 data has shown that operating cost savings in energy, chemicals and reduced RO membrane replacement rates compensate for the increased capital cost. Process selection/synthesis of the pretreatment train is certainly a matter requiring a comprehensive sustainability assessment as discussed extensively by Lattemann et al. [24], where a multi-criteria assessment (MCA) methodology is proposed. The clear environmental benefits of the membrane-based pretreatment processes, accounted for in such generalized analyses, tend to outweigh some process cost drawbacks. In fact, Fritzmann et al. [41] have estimated that a 30% smaller impact is associated with membrane filtration, compared to conventional pretreatment.

6.2.4 Main RO Desalination Section

6.2.4.1 Outline of Main RO Process Design and Operation Issues

The main part of the plant includes pumps, energy saving devices, RO membrane trains, cleaning-in-place (CIP) system, and plant monitoring facilities. Pretreated feedwater desalination takes place in the RO membrane trains, each comprised of a multitude of pressure vessels (Fig. 6.3) arranged in parallel, as discussed at length in [15]. The heart of the desalination process is the spiral wound membrane

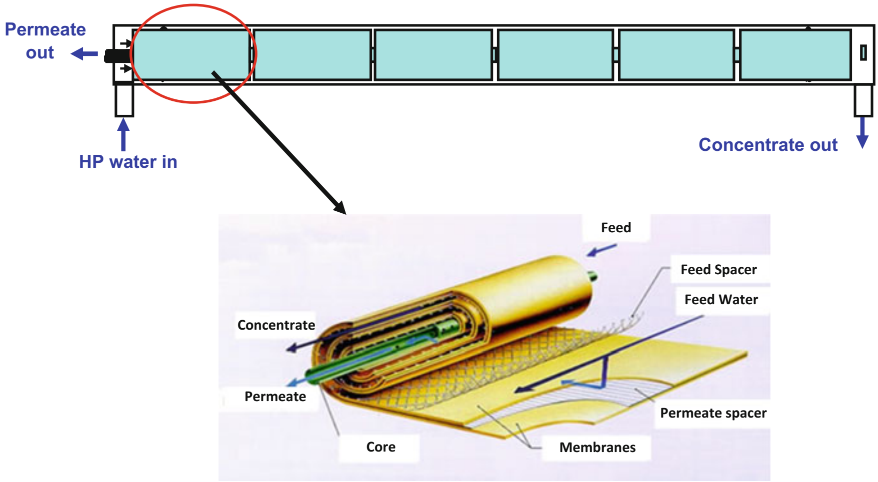

Fig. 6.3 A schematic of pressure vessel including several SWM elements, and a view of a SWM module indicating its function

(SWM) module; usually seven or eight SWM modules are connected in series within each pressure vessel (Fig. 6.3). Over the past 20 years, considerable standardization has taken place in the membrane industry, involving the use of 8-in. SWM modules [42]. There are clear economy-of-scale benefits that tend to favor building large RO plants; however, such benefits appear to be relatively insignificant for plants over 100,000 m^3/day [15]. Moreover, this assessment is made from the "narrow" perspective of a traditional techno-economic analysis, inadequately (if at all) taking into account the aforementioned broader sustainability issues. For large size RO plants employing 8-in. SWM elements, the typical production capacity of a train, employing "off-the-shelf" standard equipment, are approx. 21,000 m^3/day [15]. However, the recent introduction of large 16-in. elements has provided incentives to modify the above standard plant design (of trains with horizontally placed pressure vessels) rather drastically, by placing the large diameter pressure vessels vertically [20].

The arrangement of SWM modules in series within the pressure vessels (the latter in parallel connection comprising a train) facilitates modeling and performance analysis of a RO train and of an entire plant [43, 44]; indeed, one can deal in a detailed and comprehensive manner with a single SWM module and then predict in a rather straightforward fashion the performance of a pressure vessel and of the entire RO desalination plant [44, 45]. In dealing with a SWM module, the following main design and operating parameters are identified [46].

Design parameters

- Membrane permeability
- Physicochemical surface properties
- Geometrical characteristics of retentate-side spacers
- Membrane sheet dimensions for fixed external SWM module dimensions
- Characteristics of permeate-side fabric/spacer

Operating parameters

- Permeate flux, or imposed feed pressure, depending on desalination plant operating mode
- Cross-flow velocity at retentate side

Operating problems with spatial and temporal variability in general [43–45] are as follows:

- *Concentration polarization*
- *Fouling*; organic matter, inorganic colloids, bio-foulants depositing in the SWM channels
- *Scaling*; mainly sparingly soluble salts, silica depositing within the SWM module
- *Frictional pressure losses* in retentate and permeate channels of SWM module.

The design and operating parameters are obviously subject to optimization, within their respective range of feasible variation [46], in the context of overall RO process optimization (e.g., [47, 48]). The operating problems are of great interest to this presentation as they directly affect process performance and overall sustainability, in at least two ways; i.e., they directly affect both SEC, as analyzed in the following, and the consumption of chemicals employed for conditioning the feedwater and for periodically cleaning the RO membranes. The types and quantities of these chemicals should be fairly accurately estimated due to their impact on process cost and the environment, as discussed in the following section.

Regarding the membrane filtration process, a generalized form of the Darcy equation is applicable locally within the SWM modules [43, 46]:

$$J = \frac{P_R - P_P - \Delta\pi(C_W)}{\mu(R_m + R_C)} \tag{6.1}$$

where P_R and P_P are the local retentate- and permeate-side pressures, the term $\Delta\pi(C_w)$ represents the osmotic pressure difference across the membrane, μ is the water viscosity and R_m, R_c are the clean membrane resistance and fouling resistance, respectively; C_w is the salt species concentration at the membrane surface. The term in the numerator is the so-called net driving pressure, which is responsible (in combination with the local flux) for part of the energy spent during desalination. Other contributions to SEC include the energy spent to overcome the osmotic pressure difference and the friction losses due to flow of retentate and permeate in the respective channels of the SWM modules, discussed in the following.

The general objective *in desalination plant design and operation* is to maximize the desalinated water recovery with the minimum cost (and energy consumption), under conditions minimizing the environmental impact and satisfying all other environment-related constraints. A key objective *in designing SWM modules for particular applications* (i.e., catering to particular feedwater qualities) is to maximize the permeate flux J with the minimum imposed pressure P and energy consumption. To meet this objective, the main SWM design targets include [46]:

- Improvement of membrane properties; i.e., improved permeability, antifouling behavior.
- Reduction of friction losses (ΔP) within the narrow flow channels of SWM modules.
- Reduction of concentration polarization, i.e., increase of mass transfer to the membrane.
- Mitigation of fouling; increased shear stresses at membrane surface are considered beneficial in this respect.

6.2.4.2 Specific Energy Consumption in RO Membrane Desalination Processes

For the purpose of this presentation, a typical single-stage desalination process is considered, including concentrate energy recovery by a battery of energy recovery

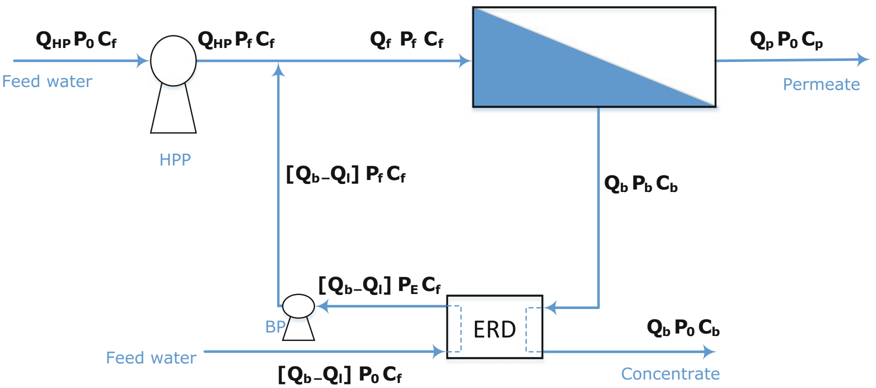

Fig. 6.4 Schematic of a single-stage membrane desalination unit with energy recovery device (ERD). Reprinted with permission from ref. [50]. Copyright © 2017 Elsevier

devices (ERD), as shown in Fig. 6.4. Pressure exchangers [10, 49] appear to hold advantages compared to other types of ERD. The variables in this process are indicated in the diagram of Fig. 6.4, and some key parameters are defined as follows:

Pressure difference across SWM vessel: $\Delta P = P_f - P_b$

Pressure transfer efficiency of ERD: $n_E \approx \frac{P_E}{P_b}$

Leakage ratio of ERD: $b = \frac{Q_l}{Q_b}$

Here Q_b and Q_l are the brine flow rate and leakage flow rate in ERD, respectively.

The SEC in kWh/m^3 is determined, by applying an energy balance over the entire process [50], as follows

$$\mathrm{SEC} = \frac{W_{\text{total}}}{Q_P} \tag{6.2}$$

$$\mathrm{SEC} = \frac{1}{R}\left[\frac{P_f - P_o}{n}\right] + (1-b)\left[\frac{1-R}{R}\right]\left[\frac{P_o + n_E \Delta P - n_E P_f}{n}\right] \tag{6.3}$$

Here W_{total} is the total hydraulic power, Q_P the process permeate flow rate, R the desalinated water recovery fraction and η the overall pump efficiency, accounting for inefficiencies of pump, electrical motor, and variable frequency drive [50].

For the case of "*ideal*" *operation of pumps and pressure exchange equipment* (i.e., $b = 0$, $\eta = \eta_E = 1.0$), the SEC under ideal conditions SEC$_i$ is given as:

$$\mathrm{SEC}_i = \left(\frac{1-R}{R}\right)(\Delta P) + \left(P_f - P_o\right) \tag{6.4}$$

Therefore, energy losses due to the nonideal pump and ERD operation, SEC$_{\text{inef}}$, are obtained from the difference of Eq. (6.3) minus (6.4), i.e.

$$\mathrm{SEC}_{\mathrm{inef}} = \mathrm{SEC} - \mathrm{SEC}_i \tag{6.5}$$

From these expressions, SEC is readily computed in Pascal or kWh/m^3, with a conversion factor 1.0 kWh/m^3 $\approx 3.6 \times 10^6$ Pa. It should be further noted that in the present treatment, two simplifications are made, with no loss of generality; i.e., that (a) the feedwater pressure at the pumps suction, as well as the permeate and concentrate discharge pressures are at the same reference value P_o (Fig. 6.4), and (b) the pressure drop in the interconnecting piping in the membrane trains is ignored.

6.2.4.3 Itemized Contributions to SEC

To assess sustainability issues of the RO desalination main process, it is necessary to determine the particular contributions to SEC due to the physicochemical and transport phenomena taking place within the SWM modules, arranged in series in the pressure vessels that comprise the main desalination facility. For a single-stage operation considered here, it is sufficient to determine SEC in a single pressure vessel, schematically shown in Fig. 6.4, with pressure and concentration of feed/inlet, brine (retentate exit) and permeate outlet streams [P_f, C_f], [P_b, C_b] and [P_o, C_p], respectively. The particular contributions to SEC are as indicated in the preceding subsection: the energy consumption to overcome the osmotic pressure, $\mathrm{SEC}_{\mathrm{os}}$, the energy consumption due to permeate filtration SEC_f, and the energy consumption due to fluid friction losses in the SWM module retentate and permeate channels, SEC_R and SEC_P, respectively; to these contributions, $\mathrm{SEC}_{\mathrm{inef}}$ is added, accounting for the energy losses due to nonideal pump and ERD operation.

Under steady-state conditions (i.e., for constant feed conditions as well as membrane properties), there is a spatial variation of all process parameters throughout the membrane sheets comprising the SWM modules. These process parameters, including local pressures, concentrations, transmembrane fluxes and velocities in the SWM channels, are required for the computation of the above-mentioned itemized contributions to SEC [50]. Recently developed advanced simulation software [43–45], capable of predicting the spatial variation of all such parameters of interest, has been employed to accurately determine the itemized SEC contributions [50]. Case study results for brackish and seawater desalination are summarized here for the *constant recovery* mode of RO plant operation.

The main variables of interest here are the pressure at retentate and permeate side (P_R and P_P, respectively), the bulk and wall concentration of salts (C_b and C_w) at the retentate side (responsible for the respective osmotic pressure of retentate) and the local permeate flux distribution J. The contributions to SEC described in the following will be expressed with respect to the total permeate flow rate Q_P, at the outlet of a pressure vessel. However, contributions to SEC can be obtained per SWM module to get insights into the variability of these parameters along the pressure vessel. The computational scheme employed [43, 44] involves finite volume elements with corresponding finite membrane surface element ΔA; thus, the flux distribution values J_i correspond to local permeate flow rates $Q_{\mathrm{Pi}} = J_i \Delta A$.

Energy consumption to overcome osmotic pressure, SEC$_{os}$
This item of energy consumption is expressed as

$$\mathrm{SEC}_{\mathrm{os}} = \frac{\sum_{i=1}^{N} Q_{\mathrm{Pi}} \Delta\pi(C_{\mathrm{wi}})}{Q_P} \tag{6.6}$$

where $\Delta\pi(C_w)_i$ is the effective osmotic pressure difference computed with the local wall concentration $(C_w)_i$ due to polarization phenomena. One can also compute a theoretical minimum $\mathrm{SEC}_{\mathrm{min}}$ corresponding to osmotic pressure of the bulk fluid, of concentration C_b; i.e., using in Eq. (6.6) the osmotic pressure distribution $\Delta\pi(C_{\mathrm{bi}})$ instead of $\Delta\pi(C_{\mathrm{wi}})$. Therefore, the expression

$$\mathrm{SEC}_{\mathrm{CP}} = \mathrm{SEC}_{\mathrm{os}} - \mathrm{SEC}_{\mathrm{min}} \tag{6.7}$$

provides a fair estimate of energy consumption due to concentration polarization.

Energy consumption due to filtration, SEC$_f$
As indicated in Eq. (6.1), SEC_f depends on the spatial distributions of local transmembrane pressure (TMP) and of the local effective osmotic pressure; i.e.,

$$\mathrm{SEC}_f = \frac{\sum_{i=1}^{N} Q_{\mathrm{Pi}} [P_{\mathrm{Ri}} - P_{\mathrm{Pi}} - \Delta\pi(C_{\mathrm{wi}})]}{Q_P} \tag{6.8}$$

However, this quantity is directly affected by the membrane permeability (or resistance R_m) which essentially determines the local flux J_{i} and Q_{Pi} through Eq. (6.1); i.e.,

$$Q_{\mathrm{Pi}} = \frac{[P_{\mathrm{Ri}} - P_{\mathrm{Pi}} - \Delta\pi(C_{\mathrm{wi}})] * \Delta A}{\mu * R_m} \tag{6.9}$$

It should be further noted here that fouling in the retentate channels affects directly SEC_f through an additional fouling resistance R_c [51] as shown in Eq. (6.1) and indirectly through the reduction of the transmembrane pressure term in the nominator of Eq. (6.9), which necessitates an increase of the feed pressure $P_f = (P_R)_{\mathrm{inlet}}$ to maintain a constant permeation rate $Q_{\mathrm{pi.}}$ The effect of fouling on SEC is discussed elsewhere [50].

Energy consumption due to friction losses in SWM module channels, SEC$_R$ and SEC$_P$
The contribution to SEC due to flow friction losses in the retentate and permeate channels is designated as SEC_R and SEC_P, respectively. These quantities can be determined through local data as in preceding cases; i.e.,

$$\mathrm{SEC}_R = \frac{\sum_{i=1}^{N} Q_{\mathrm{Ri}} \cdot \Delta P_{\mathrm{Ri}}}{Q_P} \tag{6.10}$$

$$\mathrm{SEC}_P = \frac{\sum_{i=1}^{N} q_{\mathrm{Pi}} \cdot \Delta P_{\mathrm{Pi}}}{Q_P} \tag{6.11}$$

6.2.4.4 Results of Case Studies—Comments

Detailed results of itemized SEC contributions are reported in [50] for two realistic case studies corresponding to RO desalination of sea and brackish water of salinity 40,000 and 2,000 ppm, respectively. These results are based on an earlier extensive parametric study [45]. A single-stage mode of operation with ERD, shown in Fig. 6.1, is considered. The constant recovery for sea and brackish water is taken 50 and 70%, respectively. In both cases, seven SWM elements (8-in.) per pressure vessel. Parameter values for state of the art feed- and permeate spacers as well as membrane permeabilities are considered; detailed input data, typical of those encountered in practice, are provided in [45, 50].

For convenience, pie charts are presented in Figs. 6.5 and 6.6 for seawater and brackish water desalination, respectively. The estimation of energy losses due to

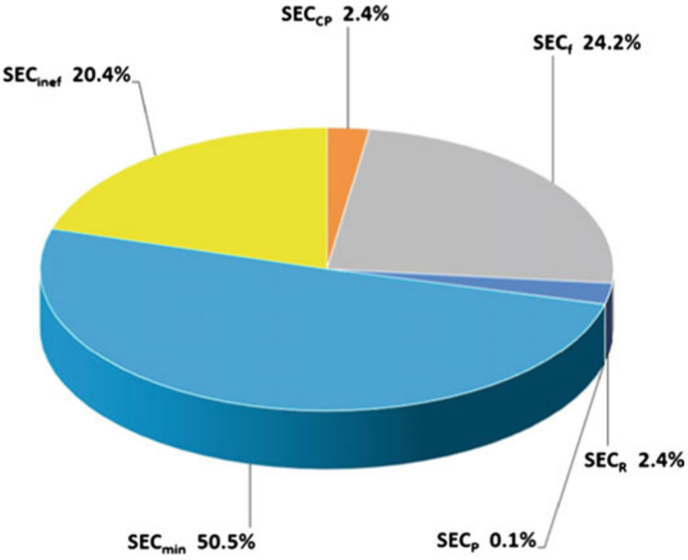

Fig. 6.5 Seawater RO desalination process at steady-state operation. Itemized percentage contributions to specific energy consumption; total RO process SEC = 2.374 kWh/m^3 [50]. Reprinted with permission from Ref. [50]. Copyright © 2017 Elsevier

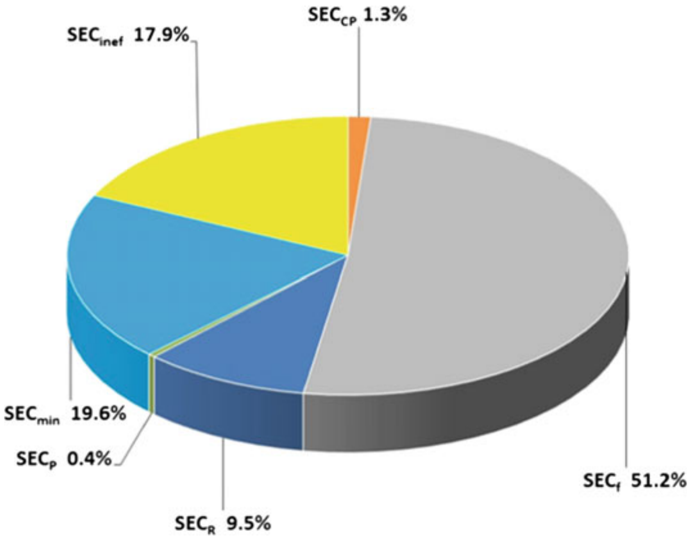

Fig. 6.6 Brackish water RO desalination process at steady state. Itemized percentage contributions to specific energy consumption; total RO process SEC = 0.379 kWh/m^3 [50]. Reprinted with permission from Ref. [50]. Copyright © 2017 Elsevier

high pressure pumps is computed by considering an overall efficiency $\eta = 0.85$, obtained as follows

$$\eta_{\mathrm{E}} = \eta_{\mathrm{hydr}} \cdot \eta_{\mathrm{motor}} \cdot \eta_{\mathrm{VDF}} \tag{6.12}$$

where the respective hydraulic pump, electrical motor and variable speed drive efficiency values $\eta_{\mathrm{hydr}} = 0.90$, $\eta_{\mathrm{motor}} = 0.96$ and $\eta_{\mathrm{VFD}} = 0.98$ [49] are typical of the performance of modern pumping systems. Regarding ERDs, state-of-the-art equipment efficiency $\eta_E = 0.95$ and leakage ratio $b = 0.02$ [10] are used in the computations.

The data depicted in Fig. 6.5 confirm the well-known significance of osmotic pressure effects on energy consumption; i.e., for this case study of seawater desalination, $\mathrm{SEC_{min}} = 1.2$ kWh/m^3, which corresponds to 50.5% of the total SEC of the RO process. However, it is interesting that the direct contributions to SEC due to flow frictional losses in both membrane channels and to concentration polarization are relatively insignificant; i.e., at the level of 2.5% of SEC for the main desalination section. This percentage is even lower if one adds to SEC the contributions from other sections of the plant; i.e., from intake, pretreatment and posttreatment sections. It is clear that the two other contributions due to pumps and ERD nonideal performance ($\mathrm{SEC_{inef}}$) and fluid filtration through the membrane (SEC_f) are of particular significance and at roughly the same level ($\sim$20–24%); these quantities also present the greatest potential for energy savings, as subsequently discussed. The total SEC in the main desalination process for seawater, determined by summing up the itemized contributions, is SEC = 2.374 kWh/m^3.

Regarding *brackish water* desalination, Fig. 6.6 reveals a very different total value and distribution of various SEC components, compared to seawater desalination. Specifically, the total SEC is almost an order of magnitude smaller than that for seawater desalination, due to the much smaller salt concentration and corresponding osmotic pressure. Further, it is interesting that the energy losses due to membrane resistance SEC_f account for half of SEC (under the conditions of this case study), with much reduced $\mathrm{SEC}_{\min}$ due to relatively small osmotic pressure. The contribution of pump and ERD inefficiencies are still significant, whereas that due to friction losses in the retentate channels SEC_R tends to become substantial ($\sim 10\%$). Despite the generally small energy consumption for this low-salinity feed fluid, improved membrane permeability appears to offer the most significant potential for reduction, and to a lesser extent reduced pump/ERD inefficiencies and friction losses at retentate side.

Comments

As it is well known, the effect of feedwater salinity is dominant, accounting for the large difference in SEC between sea and brackish water desalination. Therefore, ongoing efforts to desalinate "diluted" saline waters (e.g., by mixing seawater with lower salinity surface waters, as well as with treated effluent streams) are well justified. Such efforts are ongoing and have already been apparently successfully demonstrated (e.g., [52, 53]).

For *high-salinity feedwater*, two areas deserving particular attention for reduction of SEC are: (a) improved efficiencies of high pressure pumps and of ERD equipment and (b) membranes with improved permeability. For instance, for the case of seawater desalination, it can be readily determined [50] that increasing the pumps efficiency only by 2% leads to energy savings roughly equal to (or even greater than) the energy consumption due to total fluid friction losses in the retentate channels across the pressure vessels. Regarding energy losses due to permeate filtration, SEC_f, the ongoing efforts [7, 8, 14, 54] to increase membrane permeability while maintaining a high level of salt rejection can pay off. Improving membrane permeability has a direct impact on feed pressure P_f reduction and thus on SEC_f; moreover, by reducing P_f, proportional reduction is achieved of energy losses due to pressure equipment inefficiencies $\mathrm{SEC}_{\mathrm{inef}}$. It should be stressed, however, that the retentate osmotic pressure poses limitations to benefits resulting from permeability improvements.

A significant topic in designing and operating desalination plants, with direct and indirect impact on energy consumption, is the design of SWM elements, and in particular the *optimization of membrane envelope number (or width)* and *of feed spacer geometrical characteristics* [42, 55], for a fixed external SWM element diameter. It is well documented that fewer envelopes of longer width are associated with greater spatial nonuniformity of transmembrane pressure and of flux, entailing greater feed pressure to achieve a certain/fixed water recovery [44, 45], with obvious negative impact on SEC. Feed spacer geometry also impacts on friction losses and concentration polarization in the feed channels [44, 45, 56]; moreover, there is evidence (e.g., [57]) that it affects membrane *fouling phenomena*. In the light of the present results, it appears that the direct and indirect effects due to fouling are more important compared to energy consumption due to fluid friction losses in the SWM module channels (SEC_R and SEC_P). Indeed, an increase of the effective membrane resistance due to fouling can cause a substantial increase of SEC_f and of SEC_{CP}, which can lead to increased feed pressure (in constant recovery processes) and in turn to an increase of energy losses primarily due to pressure equipment inefficiencies SEC_{inef}. It will be also stressed that SEC_{CP} can additionally increase due to cake-enhanced osmotic pressure (CEOP) mechanism [58]. More details on quantifying the effect of fouling are given in [50]. However, it should be stressed here that advanced and reliable tools are required to monitor the performance of RO units, including predictions (or early warning) of potentially evolving (and possibly uncontrolled) fouling and scaling throughout the pressure vessels of a plant. Advanced dynamic simulators under development [59, 60], capable of predicting such evolution of fouling, could be very valuable for that purpose.

Among alternative approaches to reduce energy consumption, through reduction of feed pressure, a two-stage operation has been proposed (e.g., [14, 61],) whereby the first stage (treating the input feedwater of higher flow rates) can operate at significantly lower feed pressure; this is permissible because of the relatively smaller fluid osmotic pressure in the leading SWM elements. However, the issue of selecting process schemes (i.e., whether of single- or two-stage type, seven or eight SWM module pressure vessels, other), can be resolved through a multi-criteria optimization (e.g., [47, 48, 62]), involving (in addition to SEC) decision variables related to overall sustainability [22], i.e., product water cost and environmental impact indices; moreover, in a comprehensive desalination process optimization, one should consider at the outset other key project objectives, limitations, and local conditions; e.g., boron removal, feedwater composition and variability, available electric power and tariff variability [47, 48, 62].

6.2.4.5 Consumption of Chemicals

A variety of chemicals are used in RO desalination plants, including *biocides* (to control biofouling), *coagulants* (mostly in the feedwater pretreatment section), *scale control additives* (anti-scalants and acids for pH control) and an assortment of *cleaning chemicals*. The literature is very extensive on the various chemicals, used under prescribed protocols, mostly recommended by membrane manufacturers [15, 16] and companies specialized on membrane cleaning. Lattemann and Hoepner [63] provide a fairly thorough account of the great variety of chemicals used, their function, the likely reactions with other naturally occurring species in the feedwater and relate by-products as well as possible effects upon their release into the aquatic environment. For the purpose of this chapter, only a brief outline will be provided of the main categories of chemicals in specific sections of the RO desalination plant.

Chlorine is commonly used to control biological growth; it is injected at the intake in the form of hypochlorites of potassium and calcium, or as chlorine gas in large plants, under various protocols. Iron(III) salts (either $FeCl_3$ or $FeClSO_4$) and sulfuric acid are employed as coagulants and for pH adjustment, respectively. Sodium hypochlorite is also used in backwashing periodically the filtration system in the pretreatment section. The feedwater to the RO process units is commonly treated by adding sodium bisulfite to remove chlorine (which is harmful to the polyamide membranes) and anti-scalants; the latter is added at sufficient concentration to be effective at the tail end of pressure vessels where the concentrate becomes supersaturated in sparingly soluble salts of Ca, Ba, Mg, etc. For periodic RO membrane cleaning, a variety of protocols exist, involving acid/alkali treatment mainly to dissolve/remove inorganic scale, and various detergent formulations (mostly of proprietary composition) to remove foulants and treat the membrane surface, usually aiming to render it hydrophylic and resistant to organic fouling [54, 64]. The addition of an appropriate dose of anti-scalant in practice is routinely decided on the basis of the feedwater salinity, the plant permeate recovery and (in some cases) by running laboratory jar tests; excess anti-scalant is commonly present in the brine exiting the RO plant. Additionally, understanding the onset of scaling in RO plants is considered incomplete (e.g., [65, 66]). Therefore, there is uncertainty regarding optimum anti-scalant concentration, which should be sufficient to prevent membrane scaling while avoiding an excessive amount that is mixed in the concentrate for disposal to the environment; this is an issue to be dealt with in environmental impact assessments as some of the effective anti-scalants are harmful to the environment [67]. In Table 6.2, a list is provided of the most common chemical compounds (and respective dosages) employed in membrane desalination plants.

The cleaning frequency of a RO membrane train is an indicator of the overall performance of a RO plant, as frequent cleanings reveal problematic control of fouling and scaling. Cleaning frequency mainly depends on the quality of feedwater to RO section (i.e., on the effectiveness of the pretreatment operation) and on the appropriate operation of this section in terms of permeate flux distribution in the pressure vessels and permeate recovery level. It is fairly well known that high fluxes and high recovery, in relation to particular feedwater conditions, tend to aggravate membrane fouling [69] and possibly scaling [59, 65].

Table 6.2 Common chemicals and dosages for pretreatment and membrane cleaning of RO units

Chemical	Function	Concentration, mg/L
Chlorine	Disinfection	3
Ferric chloride	Flocculant	3
Polycarboxylate	Anti-scalant	1.05
Sodium bisulfite	Dechlorination	6
Sulphuric acid	pH adjustment	25
Sodium hypochlorite	Membrane cleaning	3

Data reported by Tarnacki et al. [68]

6.2.5 Post-treatment Section

The desalinated water through RO membranes is slightly acidic, very soft (i.e., with very low calcium and magnesium hardness), possessing low buffering capacity [70, 71]. With such characteristics, the desalinated water cannot be supplied directly for either domestic consumption and/or irrigation. Therefore, remineralization of RO permeate is necessary to provide essential ingredients (Ca, Mg, carbonates) and increase the pH, to meet health requirement and to render the distributed water palatable and noncorrosive. Water quality goals for posttreatment processes are usually site-specific, mainly depending on the water source, the particular implementation of RO membrane process and the specific quality requirements/standards of end use; for example, permeate produced by a single-pass RO process typically has greater total dissolved solids (TDS) content than permeate from a two-pass RO system.

There are comprehensive reviews on RO permeate remineralization (e.g., [70, 71]), which provide a rather thorough treatment of the methods available, the criteria for selecting an optimal post-processing scheme as well as relevant process cost data [72]. Available methods for conditioning RO permeate include [71] blending with source water, direct dosage of chemicals, dissolution of limestone, dolomite and magnesium oxide, ion exchange, and a novel process of micronized limestone dissolution. At present, on the basis of recent experience with large and medium size RO plants [70], the most commonly used posttreatment system worldwide is the sequential addition of lime and carbon dioxide. However, a problem often encountered with this method [70] is to maintain low turbidity in the treated water due to lime. Another attractive and cost-effective remineralization process, which is presently fairly common in small and medium size plants, involves calcite dissolution reactors (i.e., packed beds, also termed "calcite contactors") preceded by addition of carbon dioxide; finally, pH adjustment is commonly needed, by employing sodium hydroxide or controlled CO_2 stripping. However, it should be noted that because of the low solubility of calcite at the near-neutral pH of the desalinated water (to achieve the required calcium concentration in the final potable water), the pH is reduced to less than 4.5 [70] before the permeate enters the calcite contact tanks; sulfuric acid is employed for this pH adjustment. Another attractive variant of the aforementioned calcite dissolution process involves (instead of calcite) the use of dolomite [73], comprised of calcium and magnesium carbonate, to achieve addition of both Ca and Mg to the final water. Key data on the kinetics of dolomite dissolution and the design of such an alternative remineralization process are presented in [73].

As discussed in the following section, compared to the lime-based posttreatment systems, the calcite dissolution systems appear to have distinct advantages [71, 72]; i.e., they are less costly regarding both capital investment and material/chemicals, require less carbon dioxide, and are less susceptible to the turbidity problem associated with use of lime. At present, large-scale SWRO desalination plants employing the calcite contactor technology are located in Mediterranean countries, notably in Israel, Spain, and Cyprus, where high-quality calcite is available. However, it should be noted that lime/carbon dioxide conditioning is presently the dominant posttreatment method, which is attributed [70, 72] to lack of availability of high-quality (food grade) calcite near desalination plant locations as well as to limited experience with the use of calcite contactors for large desalination plants, with exception of Israel. Regarding sustainability assessment of the posttreatment section of RO plants, it may be argued on the basis of relevant published work [71] that it is fairly straightforward to perform it (more so than other parts of the plant), whether the lime-based method or the calcite contactor technology is used.

6.2.6 Concentrate Treatment/Disposal Facility

This part of the plant and related operations tend to become very critical during all phases of the (medium and large) SWRO desalination project development, including significant studies to support permit applications to regulatory authorities in the planning phase as well as environmental monitoring studies during plant operation. The effluents to be discharged from the RO membrane plant include the concentrate from the main desalination process, spent pretreatment-filter backwash water and membrane cleaning solutions. In the case of membrane pretreatment process (commonly operating at less than 100% recovery), the retentate of this operation as well as the respective membrane cleaning solutions have to be handled instead of the filter backwash water. The concentrate is the largest effluent stream, posing the greatest management challenge to process designers of modern desalination plants [74]. In the United States, where strict regulations exist regarding RO effluent disposal, the most commonly used management practices include (1) surface water discharge, (2) sewer disposal, (3) deep well injection, (4) land application and (5) evaporation ponds; however, similar trends are observed in RO plants worldwide. Data presented by Voutchkov [16] show that surface water discharge is the most common method for disposal of desalination plant effluents as it is convenient for practically all sizes of desalination projects located in coastal areas; it is certainly the only method practiced for large RO plants. Sewer (or wastewater collection system) disposal is the most frequently applied method for effluent disposal from small desalination plants. Deep well injection is considered as one of the most suitable methods for disposal of concentrate from inland brackish water desalination plants. Evaporation ponds and land application are brine management alternatives, mainly for relatively small-size plants, in geographic areas where climate and soil conditions are favorable. It is evident, therefore, that the selection of an appropriate RO effluent disposal method is specific to the conditions of each desalination project, and a very challenging task, with outcome subject to review, approval, and control (regarding implementation plans) by relevant authorities worldwide [16, 75–77].

Regarding the common case of surface water body discharge of concentrates, a comprehensive treatment is provided by Voutchkov [16] of all the issues to be addressed during the planning stage of a project in support of permit applications. These issues include: (1) Assessment of effluent dispersion and recirculation of the discharge plume, also in relation to the neighboring plant intake facility. (2) Evaluation of the potential toxicity characteristics of the discharged effluent. (3) Determination of the discharged effluent quality and comparison with the respective quality standards (and regulations) applicable to the point of discharge. (4) Determination of the salinity tolerance threshold of aquatic organisms for the site-specific conditions of the discharge location; this particular study is required in order to design appropriate effluent outfall geometry and conditions to achieve sufficient dilution. It should be stressed that a very significant amount of effort has to be invested [16, 74–76], involving field and laboratory studies as well as theoretical/numerical simulations to satisfy the above requirements, which entail significant delays and cost as discussed in the next section. However, such studies, if properly conducted, may accrue significant benefits in that their results can contribute to the creation of much needed databases of relevant information (see Sect. 6.4); the latter would facilitate future EIA studies and sustainability assessments [22].

In recent years, the research community has been motivated by the above practical needs and challenges, and a significant amount of work has been carried out along two main directions; i.e., (a) to achieve better understanding of the complicated interactions of synthetic micro-pollutants with the aquatic environment and (b) to develop new processes to minimize (before discharge) the volume of effluents and/or the concentration of potentially harmful compounds. Several informative reviews and critical assessments on these efforts have been published in recent years; e.g., [77–81]. In fact, the development of new methods to cope with the RO brine disposal problems is at the fore-front of R&D activities in this field.

Perez-Gonzalez et al. [81] reviewed traditional brine treatments such as evaporation and crystallization as well as other novel methods aiming to achieve zero liquid discharge and recovery of valuable compounds from these effluents; regarding the latter, there are encouraging results obtained at laboratory or pilot plant scale, not close to applications at large scale. Morillo et al. [78] presented an interesting comparative review study of brine management technologies. They dealt with methods (at various degrees of development) for reducing/eliminating brine disposal, for commercial salt recovery, brine adaptation for industrial uses and recovery of other inorganic compounds. Solar evaporation, electrodialysis, integrated processes, and brine adaptation for the chloralkali industry were included in this report. Subramani and Jacangelo [79] reviewed methods for volume reduction of RO brine, classified as membrane-based, thermal-based, or emerging technologies. The latter included forward osmosis (FO) and membrane distillation (MD) which are at the development stage. They concluded that with these methods, and combinations thereof, one can achieve nearly zero liquid discharge; however, lack of operating data at real-size demonstrations in conjunction with sustainability issues (energy etc.) are clear obstacles to applications. Joo and Tansel [80] focused on emerging contaminants (especially on newly identified ones) present in RO concentrate, for which standards and guidelines for assessment and treatment are currently lacking. A useful review was presented of various relatively novel treatment options, involving mostly hybrids of novel and available techniques; barriers to emerging treatment options were also discussed.

6.3 Sustainability Issues

6.3.1 Environmental Impact

6.3.1.1 Overview

Considering the design and operation of all sections of a RO desalination plant, outlined in the preceding section, one can recognize the following two classes of environmental impacts depending on the spatial scale of potential occurrence of such effects.

(a) *Effects at local scale*

There are two main types of potential impacts in the vicinity of RO plant operation; i.e., impacts related to the use and release to the environment (commonly to the sea in coastal areas) of *synthetic chemicals,* and impacts of continuous abstraction of large quantities of raw saline water (whether brackish or seawater) and rejection to a nearby area of the plant effluents (commonly half of those quantities in the form of concentrates). In the case of feedwater abstraction by, and effluent reinjection through, deep wells, the potential impact on aquifers is of obvious concern; at present, the latter case applies mostly to land-locked RO plants of relatively small capacity, which treat brackish water. Other impacts at local scale, to be accounted for in a comprehensive sustainability assessment, include negative and possibly positive effects on the local activities (agriculture, industry, recreation) due to operation of RO plants and the ensured availability of desalinated/potable water.

(b) *Effects at global scale*

Energy consumption in the RO plant, and the related environmental impact of electrical energy production, is the dominant issue. As discussed in the preceding section, the specific energy consumption (SEC, in kWh/m^3 of product water) is the key parameter, whose reliable determination is necessary for assessing the large-scale environmental effects (i.e., emissions of Green House Gases [GHG], climate change) and the overall sustainability of a desalination project. Additionally, the RO plant construction and operation, considered from the standpoint of comprehensive sustainability assessment, has also global-scale environmental impact due to the life cycle of equipment and other materials used; i.e., machinery, membranes, construction materials, chemicals.

In the following, the issues of energy consumption and use of chemicals/materials in the entire desalination plant will be outlined, largely based on the description of the RO facilities provided in the preceding section.

6.3.1.2 Energy Consumption in RO Desalination Plants

The total SEC in a desalination plant, of the type described in the preceding section depends on many factors related to the composition of feedwater, the particular implementation of the RO technology, the plant capacity and other local conditions.

In several publications on this topic [15, 61, 82], there is general agreement that, for the most energy demanding case of seawater desalination, SEC varies in the range ~2.8 to ~4 kWh/m^3 for medium- and large-scale plants. Voutchkov [82] confirms the above range, on the basis of data collected from 20 SWRO plants, and reports an itemized contribution to SEC by the main sections of the RO plant, depicted in Fig. 6.7; these are average values corresponding to a total SEC 3.57 of kWh/m^3. As explained in that publication, the item designated as "other facilities" roughly corresponds to energy consumed for discharging effluents; the rest correspond to the main plant sections discussed in Sect. 2.2. The dominance of the main RO desalination section that contributes by ~71% to total SEC (i.e., ~2.53 kWh/m^3) is evident. It is interesting that this value is very close to the theoretically estimated contribution to SEC for the case study [50] reported in Sect. 2.2 (i.e., ~2.37 kWh/m^3). Similar contributions to SEC from the various RO plant sections for seawater are presented in the literature (e.g., [3, 12, 13]). Despite expected variation of the percentage contributions shown in Fig. 6.7, for various reasons, the contribution due to the main section appears to be dominant and at that level [15].

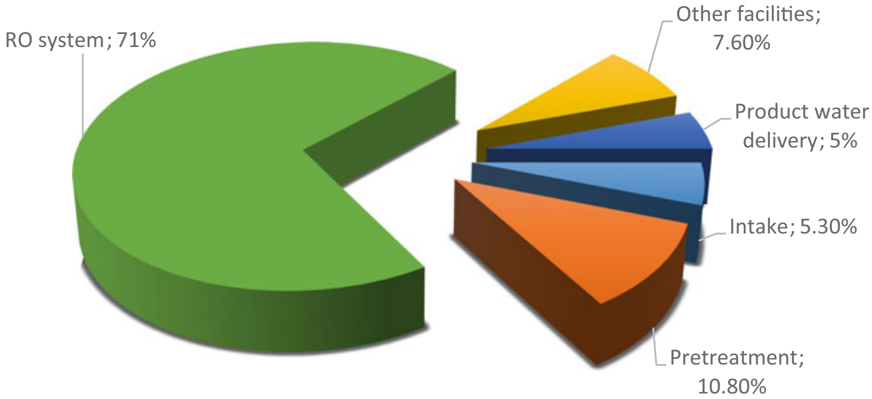

Fig. 6.7 Percentage contribution to total specific energy consumption (SEC) per section of a typical seawater RO desalination plant, from Voutchkov [82]. Total SEC = 3.57 KWh/m^3

Regarding low-salinity brackish water desalination, SEC due to the main RO section is roughly one order of magnitude smaller than that for seawater; e.g., 0.379 kWh/m^3 for the case study [50] discussed in Sect. 6.2.2. The sum of contributions to SEC from all other sections of the RO plant is smaller than that for seawater [13, 82]; therefore, for low-salinity brackish water the total SEC is less than half the SEC for seawater desalination.

Considering the present state of technology for seawater desalination, the following comments can be made upon inspection of the aforementioned itemized contributions, in connection with the analysis of SEC presented in Sect. 6.2.2: (1) The relative contribution to SEC by the main RO section is very large and there is a significant margin for SEC reduction, which is revealed in the foregoing analysis. (2) The contribution of all other sections is relatively small, with rather insignificant margin for reduction (in respect of the total SEC) due to standard equipment used in most modern plants. (3) The second largest contribution to SEC is due to the pretreatment facility, which is gaining ever greater importance [24, 36]. Moreover, the pressures to mitigate environmental impacts [24], to combat membrane fouling and improve overall plant performance and sustainability [40], appear to necessitate more elaborate membrane-based operations for raw water pretreatment (e.g., [38–40]). Therefore, significant energy savings may come from the pretreatment section only if subsurface wells are used [32], instead of the widely employed open intake facilities, currently favored in large desalination plants [16]. (4) Similar to the above arguments hold regarding energy savings from the effluents management part of the RO plant, if the current approaches of disposing of brines are still used; i.e., improved measures (effluent post-processing/handling) to mitigate overall environmental impact would not necessarily lead to reduced SEC in that section. (5) An interesting possibility exists to recover some energy from the RO concentrates by employing pressure retarded osmosis (PRO), thus achieving some reduction of total SEC; in this membrane-based osmotic process [83], brine is brought in indirect contact with either seawater or low-salinity municipal/other effluents, which might also have some environmental benefits regarding the quality of effluents, in addition to power generation. However, this technology is still under development with unforeseeable future regarding large-scale applications [84].

It is significant to point out that the above total SEC estimates may not be conservative in that they represent nearly steady-state operation of well-designed and functioning plants. However, the inherent problems of membrane performance degradation mainly due to material aging (caused by repeated chemical cleanings) and fouling, usually lead to membrane permeability reduction and feed pressure increase (to maintain constant recovery). Therefore, SEC tends to increase, during the lifetime of membranes, for reasons discussed in Sect. 6.2.2. The industrial practice is to implement a program of periodic replacement of aging membranes, in an effort to maintain nearly constant productivity of an entire membrane train and plant.

6.3.1.3 Environmental Impact of SEC

At present (and in the near future), the electrical power required for the medium and large RO plants is generated by consuming available fossil fuels; therefore, there is great concern about greenhouse gas (GHG) emissions related to power production. It is enlightening, and necessary for sustainability assessments, to estimate the environmental load due to SEC required to desalinate water. By employing typical data for CO_2 produced per kWh of generated electricity, for various fossil fuels (listed in Table 6.3), one can estimate fairly accurately the CO_2 produced per m^3 of desalinated water. For instance, for a large-scale seawater RO desalination facility, powered by a natural gas burning plant, operating with SEC approx. 3.5 kWh per $\mathbf{m^3}$ of desalinated water, the corresponding CO_2 is 4.27 lb or 1.94 kg per $\mathbf{m^3}$ of desalinated water. This is a minimum, for well operating plants under steady conditions (which is very seldom the case); i.e., (a) if cheap lignite is used, these figures are almost double; (b) if membrane fouling occurs the environmental burden is significantly rising. In this respect it is interesting that, on the basis of data from SWRO desalination plants operating in Australia, the CO_2 emissions are estimated to be double the above (essentially minimum) figure, i.e., 3.89 kg CO_2 per m^3 of product water.

6.3.1.4 Chemicals, Materials, Membranes

Chemicals and Operating materials are mainly required for feedwater pretreatment (coagulants, oxidants, other additives, depending on the type of the pretreatment operation [15, 16]) as well as in the main part of RO plant, i.e., chemicals for membrane cleaning (alkali and acid solutions, detergents), anti-scalants, biocides. Discharge of large amounts of concentrates containing an assortment of such chemicals into the coastal waters can result in significant ecological imbalances;

Table 6.3 Carbon dioxide produced per kWh of generated electricity using fossil fuels

Fuel	lbs CO_2 per million Btu	Heat rate[a], Btu per kWh	kg CO_2 per kWh
Coal			
Bituminous	205,691	10,080	0.938
Sub-bituminous	214,289	10,080	0.980
Lignite	215,392	10,080	0.984
Natural gas	116,999	10,408	0.553
Distillate oil (No. 2)	161,290	10,156	0.744
Residual oil (No. 6)	173,702	10,156	0.798

Data from US Energy Information Administration [85]. https://www.eia.gov/tools/faqs/faq.cfm?id=74&t=11

[a] Average heat rate for steam-electric generators (2014 data)

in particular, biocides such as chlorine may acutely affect nontarget organisms. The volume of discharged concentrates from large and medium SWRO plants (with a concentration factor 1.25–2.0 for 30–50% recovery) is large (in addition to pollutants present), whereas the BWRO plants (operating with a concentration factor 2.5–7.0 for 60–85% recovery) discharge smaller volume of concentrates with quite high pollutants concentration. Both types of effluents can have detrimental effects on the aquatic life and coastal the environment. Table 6.4 provides an overview of SWRO plant concentrate characteristics, including salinity, temperature, and various chemicals used for coagulation, biocides for controlling biological growth, anti-foaming, anticorrosion, and cleaning chemicals as well as an indication of the potential environmental/ecological impacts. It should be added that the continuous abstraction of seawater and discharge of effluents at a specific location (especially in the cases of open intake and surface water discharge) may also affect in the long run the quality of raw feedwater [16, 24].

*Membranes and other construction material*s. In recent years, the guaranteed (at least by some manufacturers) 5–10 years lifetime of RO membranes and the tendency to standardize construction of medium and large RO plants [15], render this issue of materials (in respect of sustainability) less crucial than 15–20 years ago, notwithstanding its significance in an integrated sustainability assessment and the related concerns by the desalination industry and authorities on the fate of discarded membrane modules. It should be noted, however, that the research community has been already dealing with this issue for several years (e.g., [87]). Renewed emphasis has been recently given to utilization, of removed SWM elements from RO plants, in some other similar applications, such as in UF/MF filtration after an extra treatment (e.g., [88, 89]), or for prolonging the good performance of RO membranes that commonly suffer degradation by cleaning oxidizing chemicals [90, 91]. It should be stressed, however, that, even if such efforts are proven successful, the issue of dealing with used SWM modules remains and should be considered in LCA studies [92].

6.3.2 Economics

6.3.2.1 Overview

Detailed cost estimates of the desalination project (of specified accuracy) are obviously extremely important for several reasons, including techno-economic assessment of process design alternatives, product water unit cost for pricing water distributed to consumers, determination of capital requirements, and certainly sustainability analyses. Detailed and reliable economic analyses, relating specific parts and aspects of process and plant design, construction and operation to respective cost parameters are also valuable to process developers and researchers because they help them assess and prioritize those aspects and issues of the project/process that need attention to achieve desirable improvements.

Table 6.4 Potential ecological/environmental impacts of the seawater RO desalination plant concentrates

RO plant concentrate—potentially harmful conditions and contained species		Environmental/ecological impacts
Physical properties		
Salinity and temperature	Up to 65,000–85,000 mg/L ambient seawater temperature	Can be harmful; reduces vitality, biodiversity at higher values; harmless after good dilution
Plume density	Negatively buoyant	Can be harmful; can have local impact on biodiversity
Dissolved oxygen (DO)	*Well intakes*: typically below ambient seawater DO due to low DO content of the source water *Open intakes*: approximately the same as the ambient seawater DO Concentration	
Biofouling control additives and by-products		
Chlorine	If chlorine or other oxidants are used to control biofouling, these are typically neutralized before the water enters the membranes to prevent membrane damage	Very toxic for many organisms in the mixing zone, but rapidly degraded, THM—RO—MSF
Halogenated organics	Typically low content below harmful levels	Carcinogenic effects; possible chronic effects, more persistent, dispersal with currents, main route of loss is thorough evaporation
Removal of suspended solids		
Coagulants (e.g., iron-III-chloride)	May be present if source water is conditioned and the filter backwash water is not treated. May cause effluent coloration if not equalized prior to discharge	Nontoxic; increased local Turbidity → may disturb photosynthesis; possible accumulation in sediments
Coagulants, e.g., polyacrylamide	May be present if source water is conditioned and the filter backwash water is not treated	
Scale control additives		
Anti-scalants acid (H2SO4)	Not present (reacts with seawater to cause harmless compounds, i.e., water and sulfates; the acidity is consumed by the naturally alkaline seawater, so that the discharge pH is typically similar or lower than that of ambient seawater). Typically low content below toxic levels	Poor or moderate degradability + high total loads → accumulation, chronic effects, unknown side effects
Foam control additives		
Anti-foaming; e.g., polyglycol	Not present (treatment not required)	Nontoxic in concentration levels; good degradability

(continued)

Table 6.4 (continued)

RO plant concentrate—potentially harmful conditions and contained species		Environmental/ecological impacts
Contaminants due to corrosion		
Heavy metals	May contain elevated levels of Fe, Cr, Ni, Mo if low-quality stainless steel is used	Only traces; partly natural in the sea; no toxic or long-term effects
Cleaning chemicals		
Cleaning chemicals	Alkaline (pH 11–12) or acidic (pH 2–3) solutions with additives: detergents (e.g., dodecylsulfate), complexing agents (e.g., EDTA), oxidants (e.g., sodium perborate), biocides (e.g., formaldehyde)	Highly acidic/alkaline solutions may be toxic unless neutralized. Disinfectants highly toxic at very low concentrations, detergents moderately toxic; complexing agents very poorly degradable

Data from Lattemann and Hoepner [23] and Dawoud and Al Mulla [86]

The methodology of economic analysis of desalination projects does not differ from that employed in usual projects involving implementation of physicochemical processes; as it is well known, such methodologies require a significant degree of equipment standardization and rely, among other information, on various types of cost data (on equipment, materials, processes, etc.) that are gathered over a sufficient number of years of operating similar plants and processes. However, the RO desalination industry is relatively "young" and has rapidly evolved (and still evolving) within a relatively short period of time, i.e., in the past 15–20 years [1, 4, 15]; thus, uncertainties and a rather incomplete database exist. Typical of the uncertainties encountered by plant designers are those related to RO membrane performance parameters, membrane effective lifetime and cost, which have not stabilized yet, mainly due to the pursued (and potential) improvements [7, 8, 54]. Other such uncertainties (due to technical progress) are related to modification of SWM module dimensions and RO plant equipment outlay, due to the introduction of large (16-in.) SWM elements in connection with the vertical pressure vessel arrangement in large new plans [20]. Therefore, one can observe that there is still a need for standardization of equipment and practices as well as for more complete databases, which are essential for reliable cost/economic analyses and for project development. It should be mentioned, however, that successful efforts have been made to establish some standard designs and RO plant construction with modular units, by employing off-the shelf items of standard function and known lifetime [15, 16]. Another related issue is the availability of reliable, well-documented, and transparent computational tools for plant design and related cost analysis. In fact, those involved at depth in economic analyses and sustainability assessments (e.g., [22]) consider the lack of such tools one of the major impediments in implementing assessments in a reliable manner.

6.3.2.2 Product Water Unit Cost

The key parameter in desalination projects is the product water unit cost (PUC), expressed in monetary units per m^3 (commonly US$/$m^3$). This quantity is comprised of two general cost categories; i.e., capital related expenses, and operation and maintenance (O&M) costs. Capital costs comprise all expenses to realize the project since the initial planning stage, to construct the physical plant and to finance the project. Operation and maintenance (O&M) costs include all expenditures associated with RO plant *operation* (energy, chemicals, labor, and materials such as cartridge filters and membrane replacement), *maintenance* of plant equipment, buildings, and utilities as well as costs for compliance with various requirements for plant operation and environmental monitoring as well as other related management expenses [16]. PUC is typically computed as the ratio of annual expenses (i.e., O&M costs plus annualized capital expenses) over the produced water volume (m^3/year). Desalination costs vary in a wide range, affected by several site-specific factors, which do not allow in general extrapolations from one project to another. The single most important process parameter that determines the feed pressure level, as well as the level of PUC, is the feedwater salinity, as already discussed in preceding sections. Consequently, Voutchkov [16] has presented a thorough cost analysis of desalination projects by dividing RO plants into three broad categories, based on feedwater salinity, as follows:

1. *Brackish water of low salinity*, with TDS concentration ~500 to ~2500 mg/L. If the feedwater composition allows, it is usual to blend a certain percentage of the source water with the permeate to condition the final treated water for distribution. Such RO plants (comprising single-pass RO trains) are relatively simple to design and operate and do not present particular environmental problems. A significant number of such plants treating brackish groundwater operate in the USA (Florida and Texas [16]).
2. *Brackish water of high salinity,* with TDS concentration ~2500 to ~10,000 mg/L. The main difference from the above case, impacting on PUC, is the increased SEC due to greater salinity and osmotic pressure.
3. *Seawater*. The design and PUC of SWRO plants depends on composition of feedwater, local conditions and product water specifications. This case is discussed further below.

It will be noted that the energy issues are discussed in Sect. 6.2.2 in terms of two typical case studies for brackish and seawater, which correspond to the above cases 1 and 3.

Table 6.5 includes PUC data reported by Lapuente et al. [5] for medium- and large-scale desalination plants in Spain. It is interesting that, although there are some variations among plants, for both capital and O&M costs, the difference from the respective overall average number is quite modest. The percentage contribution of the particular cost items to PUC, depicted in Fig. 6.8, is fairly typical of SWRO plants, and in general agreement with similar data reported in many other

Table 6.5 Cost of desalinated water in the Sequra River Basin, Spain [5]

Desalination plant	Capacity (m^3/d)	Capital cost (€/m^3)	Operating and maintenance (€/m^3)
Aguilas	210,000	0.216	0.443
Alicante I	65,000	0.258	0.401
Alicante II	65,000	0.292	0.382
San Pedro del Pinatar I	65,000	0.219	0.381
San Pedro del Pinatar II	65,000	0.291	0.382
Torrevieja	240,000	0.258	0.424
Valdelentisco	140,000	0.262	0.428
Average		0.257	0.406

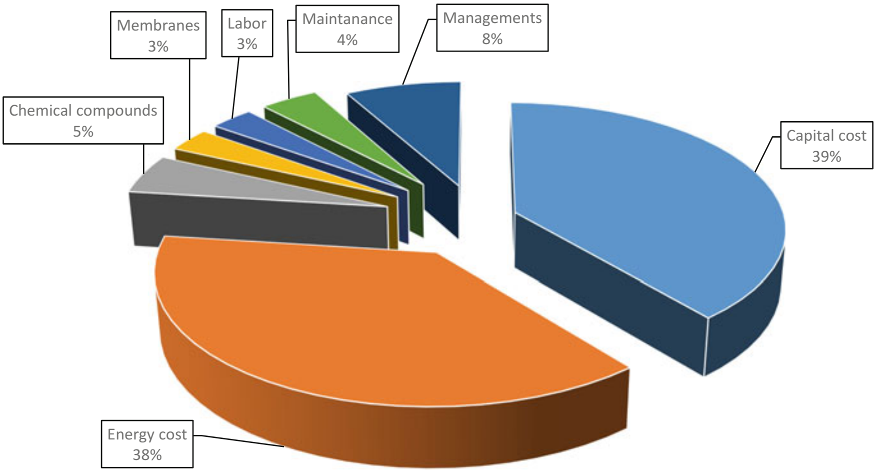

Fig. 6.8 Seawater desalination. Percent contributions of the various cost items to product water unit cost data from Lapuente [5]. Average PUC = 0.663 €/m^3

publications treating this topic [5, 93, 94]. The following comments can be made on the basis of these data: (1) Capital and energy costs are at the same high level, their sum comprising ~77% of PUC. [15] It is, therefore, significant to examine the margin and extent to which each one of these two major cost components can be reduced. Regarding energy consumption, improved efficiency of pumps and ERD as well as membrane permeability improvements have emerged as potential areas for PUC reduction (Sect. 6.2.2); comments on possible capital expense reductions follow. (2) Other than energy, the rest of the O&M cost items comprise 25–30% of PUC; although substantial in total, the individual cost items are generally fixed with narrow margin for reductions. (3) The membrane cost, including replacement, has quite modest contribution at the level 3–5%, which is attributed to significant price reduction in recent years as well as significant prolongation of membrane useful lifetime [7, 9, 15]. (4) The cost of chemicals is also relatively small; however, it is important to note that despite the small direct cost of chemicals, their potential environmental impact incurs additional costs indirectly (in equipment and operating expenses for their mitigation) and should be accounted for through a carefully selected weighting factor in sustainability assessments [22], which is likely greatly disproportionate to their direct cost contribution.

6.3.2.3 Capital Cost

For the scope of this chapter, the important case of seawater desalination will be examined. The typical case is considered of a large or medium desalination plant, commonly with open intake and raw water requiring significant pretreatment, which is designated [15] as "high-complexity project". Average values are used in Table 6.6 of the various capital cost items reported by Voutchkov (Table 18.5, [15]). The description of some direct capital cost items (marked in bold letters in Table 6.6) matches that of the main RO plant sections discussed in Sect. 6.2, although clarifications (as follows) are needed for the other capital cost items.

Table 6.6 Itemized capital costs of a RO seawater desalination project; average percentage values for a "high-complexity project" [15]

Cost item	Percentage of total capital cost	
A. Direct (construction) capital costs		
1. Site preparation	1.0	
2. Intake	4.0	
3. Pretreatment	7.0	
4. RO system equipment	33.3	
5. Posttreatment	1.5	
6. Concentrate disposal	2.5	
7. Waste and solids handling	1.0	
8. Electrical and instrumentation system	1.7	
9. Auxiliary/service equipment and utilities	1.5	
10. Buildings	4.0	
11. Start-up, commissioning	1.5	
Subtotal direct capital costs		**59**
B. Project engineering	11.0	
C. Project development	9.0	
D. Project financing	13.0	
E. Contingencies	8.0	
Subtotal indirect capital costs		**41**
Total capital costs		**100**

Useful observations can be made by inspecting the cost items listed in Table 6.6:

(1) The *direct* capital expenses at the level of 60% are typical of complicated, rather large projects [15, 16]. This percent contribution is considered modest (compared to simpler/smaller plants) not because the direct costs are modest in absolute terms, but because the respective indirect costs are quite high; for instance (indirect) project development costs (item C) are high for significant new projects, involving environmental permitting (e.g., [24]) and related costs for special studies, legal services, etc. Valid environmental concerns and lack of experience (on the "novel" RO desalination technologies and plants) by the permit-granting authorities, tend to complicate matters, leading to time-consuming procedures, thus significantly increasing such cost items including project financing (item D). It should be added, that (for the above reasons) in the simpler, "low complexity" projects, the total direct capital costs are usually significantly higher; i.e., 70–85% (Table 18.5, Ref. [15]).

(2) The main RO facility has the greatest contribution to the direct capital costs; indeed, in addition to the RO equipment costs ($\sim$33%, item #4), the greatest part of items #8 and #10 (for instrumentation/electrical systems and buildings, respectively) can be allocated to the main RO facility. Consequently, this main part of the plant should be the focus of studies aiming to reduce capital expenses and PUC.

(3) Among the items related to the other sections of the plant (#2, #3, #5, #6), the one representing construction costs for pretreatment facilities is significant. Furthermore, it should be expected that this cost item as well as the ones for the intake facility and concentrate disposal will likely have a greater contribution in future projects, due to the ever greater emphasis placed on reducing environmental impact.

(4) The rest of the direct capital cost items (#1, #7, #9, #11) represent small and fixed contributions, with no margin for reduction.

(5) As outlined in foregoing comment, the total indirect capital costs are quite high in both absolute and relative terms, especially for large projects. Therefore, it is challenging to take steps to reduce them, which would lead to PUC reduction as well.

6.3.3 Comments on Sustainability Assessment of RO Projects

The issues (environmental, economic and social) involved in sustainability assessments of RO desalination plants are outlined in Sect. 1.3. A holistic approach to perform sustainability assessments (accounting for all these issues in an equitable manner), of the type proposed by Lior [22], is highly desirable as it can provide valuable information to stakeholders, including the scientific/technical community, regulatory authorities, and society at large. However, such a comprehensive methodology, involving numerous indicators to characterize various effects, leading to quantitative results in terms of a composite sustainability index (CSI), is very difficult to implement at present for several reasons [22], including lack of standardization of the methodology, and of an adequate database of the required metrics, as well as of sound normalization procedures. Nevertheless, the general approach based on CSI computation is often implemented by using multi-criteria analysis (MCA) techniques [95], which provide a theoretical framework for dealing with the complicated effects and interactions due to the aforementioned issues. Studies employing such approaches to assess sustainability, in sectors and endeavors of lesser complexity than the large RO desalination projects, have been reported in the fields of energy [96], manufacturing industries [97], and in the selection of technologies for secondary wastewater treatment [98] and for tertiary treatment for water recycling [99].

Other presently employed methods to assess desalination plant impacts include the Environmental Impact Assessment (EIA), life cycle assessment (LCA), best available technology (BAT), and the Driver-Pressure-State-Impact-Response (DPSIR) method, which are reviewed by Lior [22]; the former two are the most frequently used methods and in particular EIA. For the comprehensive environmental impact assessment of RO plants, and in general of any type of desalination projects, the United Nations Environment Programme released in 2008 an EIA Guidance Manual [76]. The EIA contents and procedure, described in [75] and [76] involve ten basic steps which provide a rather inclusive framework of assessment for decision-making purposes. It should be noted that this type of EIA includes, in addition to identification and evaluation, development of means for mitigating the potential impacts. Lately, the adaptation of ISO 14001:2004 "Environmental management systems—Requirements with guidance for use" also gains ground for guiding EIA. A critique of weaknesses of EIAs is presented in [22]. Regarding LCA, Zhou et al. [100] provide an extensive critical review on the methodology as implemented for desalination, where they identify two types of weaknesses in need for improvement; i.e., issues related to *feasibility,* comprising the accounting methods, the supporting databases and methodological weaknesses, and to *reliability* (or uncertainty of the results) due to incompleteness of system boundary definition, unrepresentativeness of databases and lack of uncertainty analysis.

A significant, time-consuming and rather costly activity in desalination project development is the required by authorities "environmental review and permitting" in the early phases of the project, as discussed in the comprehensive treatment by Voutchkov [16], where emphasis is placed on laws, regulations, and practices in the USA. It is evident that the pressures by societies in various countries for environmental protection, provide a strong driving force (through legislation) to improve the comprehensiveness and reliability of impact assessments. Perhaps more important, in the context of this discussion, is the fact that through the permitting procedures aiming to satisfy regulations, significant studies are carried out and valuable data are collected, thus, contributing to the creation and completeness of much needed databases on environmental impact by desalination. For instance, from an overview of the regulatory framework in the USA [16] it is evident that rather extensive studies are required to secure the various permits. Indeed, to get a permit only for an "open intake" type of facility (discussed in preceding Sect. 6.2.2) an "Impingement and Entrainment Study" is required. This document requires the completion of a 12-month study, which involves collection of source water samples in the vicinity of the intake, usually two to four times per month, in order to determine the daily and annual amounts of marine organisms that could potentially be impinged on the source water intake equipment and entrained into the desalination plant. Similarly stringent requirements hold (in the form of studies) in the USA to get the *"National Pollutant Discharge Elimination System (NPDES)*" permit for concentrate disposal to surface waters in the ocean.

Finally, the following comments can be made by contrasting the above observations on the state of the art regarding environmental (or sustainability) assessment, and on the related requirements of regulatory authorities to grant permits for desalination projects, with the general conclusions drawn from the preceding discussion (in Sect. 6.2) of technical, energy, and environment-related issues of RO plant design and operation. The comparatively more difficult and important (from the sustainability point of view) case of seawater desalination is dealt with.

1. The main RO process section of the plant contributes directly by more than 50% to the product water unit cost (PUC), through energy consumption and direct capital expenses. The RO membrane technology involved tends to reach maturity, although there is still evolution and improvements made; this situation reflects progress made in recent years in designing and operating membrane modules and entire RO units. Moreover, operating and materials costs (notably those of membranes) for the RO process tend to remain stable. Additionally, a significant amount of various data have been collected on the RO process design, operation, and economics, although the respective databases are not considered sufficiently complete. In general, regarding technical and cost information needed to perform a sustainability analysis, this important part of the RO plant is not particularly problematic.
2. Regarding environmental impact, the main RO process section has a significant share mainly due to energy and chemicals consumed, that burden the atmosphere and the coastal areas, respectively. Technical issues have been identified where there is margin for improvements leading to SEC reduction; also, the quantification of SEC impact in the sustainability analysis can be readily made. However, the chemicals, despite their small contribution to PUC, have significant and difficult to quantify impact.
3. The sections of the plant where pretreatment of feedwater and posttreatment of permeate take place are fairly mature technologically, with modest contribution to the PUC. However, membrane-based pretreatment appears to need particular attention for operating improvements, which are intimately related to the good performance of the main RO part (i.e., controlling fouling/scaling).

4. The sections of raw water intake and effluent management/discharge are the most problematic from the point of view of sustainability assessment. Although there are no particular technical issues for the implementation of various options (e.g., open versus subsurface intake) and their direct contribution to PUC is relatively small and readily predictable, the environmental impact assessment presents great difficulties as it is associated with significant uncertainties regarding short and (particularly) long-term effects on the local biota. This uncertainty is due to the *ex ante* type of appraisal involved in the EIA studies combined with the paucity of data on such effects.

6.4 Current Trends and Perspectives

6.4.1 Brief Overall Assessment

The following brief assessment is made for the relatively more significant case of seawater RO desalination.

Economic issues
Regarding product water unit cost (a key metric for various assessments), *energy* and *capital expenses* dominate, with contributions at the level of ~40% each, but varying, mainly due to local conditions, plant capacity, energy sources availability.

Itemized cost per RO plant section: The main RO desalination facility dominates, contributing by more than 70% to the total product water unit cost in most cases of large RO plants.

Environmental issues
Effects at small/local scale: The seawater intake and brine disposal issues clearly dominate due to their potential negative impact on the coastal area waters and local biota. The environmental impact of the other plant sections is rather indirect, largely dependent on the quality of feedwater pumped to the inland plant for pretreatment and RO desalination. Regarding environmental issues, it should be observed that a rather strong sequential interaction exists between the various plant sections. Specifically, the design/operation of intake facilities and the quality of the pumped raw seawater significantly affects the design and performance of the pretreatment section, which (in turn) strongly affects the performance of the following RO process units; the performance of the latter (through chemicals used, frequency of membrane cleaning, etc.) determines the characteristics of the exit streams, and in particular that of brine, which can potentially impact on the local environment.

Effects at large scale: Clearly the specific energy consumption (SEC, in kWh/m^3 of product water) is the key parameter whose reliable determination is necessary for assessing the large-scale environmental effects (GHG emissions, climate change) and overall sustainability of a desalination project. Determination of the itemized contribution of various plant sections to SEC shows that the main RO process units consume the greatest part of energy per m^3 of product water. Particular factors currently contributing significantly to SEC, with a potential for reduction of energy (and margin for improvement), are mainly the efficiencies of pumps and ERDs as well as the RO membrane permeability. Efforts are also required to optimize the membrane module (focused on the feed spacer geometry) and the overall plant design, mainly to control fouling.

Sustainability assessment

An all-inclusive sustainability assessment methodology is needed, for significant RO desalination projects, providing reliable quantitative results. Such methods (notably those to determine a Composite Sustainability Index—CSI) have been proposed and demonstrated in projects of somewhat lesser significance, compared to large RO projects. However, they are difficult to implement in the latter for several reasons, including lack of standardization of methodology, problems with the normalization of various metrics representing dissimilar impacts, in the context of a computational framework, inadequacy of databases for the various indicators/metrics. The greatest difficulties are encountered in dealing with issues of abstraction of large quantities of seawater and discharge to the environment of smaller (but still significant) quantities of concentrates that contain chemicals of potential long-term environmental impact.

At present, EIA studies (with some variations depending on local environmental laws and regulations) are carried out in practically all major RO projects. Although useful experience has been gained by EIA studies, there are weaknesses and uncertainties similar to those outlined above for general sustainability assessments, especially related to raw water intake and effluent discharge. The reliability of LCA study results also seems to be compromised by inadequate databases, methodological, and other problems. Regarding environmental impact studies, required by permit-granting authorities (notably in the United States), it is interesting to note that for each particular issue (i.e., impact of intake facility, specific effluent management method) fairly demanding studies need to be prepared, involving field work and related experimental studies. One hopes that many such studies, with reliable data, will tend to enrich the respective and much needed databanks. Similarly, required systematic monitoring of RO plant operation can yield valuable data.

6.4.2 Prioritization of R&D Needs

The preceding assessment of the main technical, economic, and environmental issues, in respect of RO desalination plant sustainability, allows to suggest the following priority areas and targets for R&D activity.

Main RO process

- Improved efficiency of high pressure pumps and of energy recovery devices, in conjunction with overall optimization of plant design (i.e., optimum equipment layout), due to potential for reduced energy-related and capital expenses.
- Improvement of RO membrane permeability and fouling mitigation characteristics, aiming at reduced SEC and environmental load caused by cleaning chemicals.
- Optimization of SWM module design (focused on the feed spacer geometry) with emphasis on fouling minimization, due to potential benefits in SEC and environmental protection.
- Improved RO process monitoring tools, including advanced process simulators, for early identification of rapidly evolving and uncontrolled fouling and scaling, with expected environmental and cost benefits.
- Development of effective "green" chemicals (e.g., anti-scalants, oxidants, coagulants, cleaning compounds) to minimize environmental impact.

Intake section and concentrate handling

- Improved understanding of subsurface well/system design, construction, and operation (including impact on the local ecosystem), with expected potential sustainability benefits due to the fair quality of abstracted raw feedwater, compared to open seawater intakes.
- Improved understanding regarding the environmental impact of open intake facilities. Development of a comprehensive databank including data on various impacts on the local ecosystem.
- Development of novel processes (MD, ED, CDI, PRO, etc.) aiming to reduce the volume of discharged effluents, and the pollutants concentration, and/or utilize the brine to recover energy (through PRO) or marketable minerals/salts.

Sustainability assessment methodology

- Development of an integrated, comprehensive sustainability assessment methodology along the lines of recent studies on the subject. Issues of method standardization, normalization of the numerous indicators representing various impacts, simplifications, etc., should be addressed.
- Adequate databases should be developed on all aspects and issues accounted for (and in support of) the sustainability assessment methods. Reliable data and study reports prepared by the desalination industry to get permits from authorities as well as reports from systematic monitoring studies could be collected to enrich such databanks.
- Advanced computational tools are needed to facilitate sustainability assessment studies.

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Chapter 7
Membrane Distillation in Desalination and Water Treatment

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Abstract Membrane distillation (MD) is a thermally driven separation process. There are four types of MD: direct contact membrane distillation (DCMD), vacuum membrane distillation (VMD), air gap membrane distillation (AGMD) and sweep gas membrane distillation (SGMD). MD process has a number of potential advantages, namely, low operating temperature and hydraulic pressure, very high rejection of nonvolatile solutes, smaller footprint and potentially high water vapor flux for example in DCMD compared to conventional thermal distillation processes. For such reasons, MD has been considered as an emerging new technology in desalination and wastewater treatment. This chapter addresses a variety of applications of MD employing primarily the techniques of DCMD, VMD, and AGMD. State-of-the-art research results in different areas such as, desalination of seawater and brackish water, produced water treatment from oil exploration and coal seam gas production, high temperature DCMD, water treatment in bioreactors and oily wastewaters, treatment of processing streams from dairy, food, beverage industries and animal husbandry, concentration of acids, membrane distillation in biorefineries, mineral recovery and radioactive water treatment, are briefly presented and discussed in this chapter.

Keywords Membrane distillation (MD) applications · Direct contact MD · Vacuum MD · Air gap MD · Desalination of seawater and brackish water · Produced water treatment · High-temperature DCMD · Membrane distillation bioreactor · MD water treatment of radioactive water, biorefinery water, and for mineral recovery · MD in dairy, food, beverage, and animal husbandry industries

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7.1 Introduction

Membrane distillation (MD) based separation of a volatile species present in a heated solution is driven by a transmembrane partial pressure difference of the species being transferred through a hydrophobic microporous membrane. The membrane pores are gas-filled and are not wetted. Any volatile species can be removed thus from the feed solution. Although some attention has been paid to the removal of volatile species such as ethanol, overwhelming attention has been directed to recovering/removing water from various aqueous solutions. The most intensively studied application has been desalination.

The transmembrane partial pressure difference of water across the membrane from the hot feed solution is achieved in a variety of ways (Fig. 7.1). When a cold distilled water stream is passed on the other side to develop a lower partial pressure of water, we have *direct contact membrane distillation* (DCMD). When a vacuum is pulled on the other side, *vacuum membrane distillation* (VMD) takes place. By placing a cold surface for condensation of water vapor diffusing through the membrane pores through an additional airgap, *air gap membrane distillation* (AGMD) is implemented. One can sweep away the water vapor diffusing through the membrane pores as it emerges by a noncondensable gas and achieve *sweep gas membrane distillation* (SGMD). In both VMD and SGMD, an external condenser is needed to condense the water vapor.

A number of reviews have appeared in the literature starting with an early introduction to the four MD processes [1]. More comprehensive reviews are by Lawson and Lloyd [2], Alklaibi and Lior [3], Drioli et al. [4] and Camacho et al. [5]. These reviews generally have a much greater focus on DCMD which has been investigated much more than the other techniques. One of the earliest studies in AGMD including modeling was by Gostoli and Sarti [6].

Membrane distillation processes have attracted attention for a variety of reasons. Let us focus on water for example as the volatile species being removed from say, saline water. *First*, the vapor pressure reduction of water with increasing salt concentration is limited. As a result the vapor pressure reduction of say, a 10% salt solution is quite low around 6% [7]. This is unlike the osmotic pressure of saline

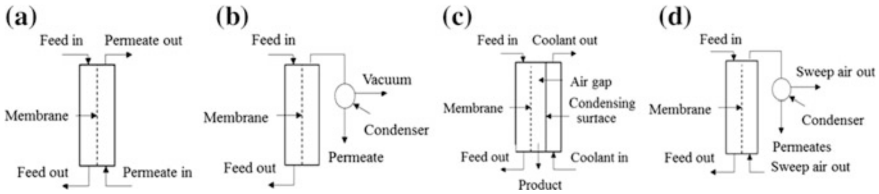

Fig. 7.1 Four types of membrane distillation (MD): **a** Direct contact MD (DCMD); **b** Vacuum MD (VMD); **c** Air gap MD (AGMD); **d** Sweep gas MD (SGMD)

water which becomes very high with 10% salt; that is why in seawater desalination by reverse osmosis (RO), the upper limit of salt concentration in brine for RO treatment at 800–1000 psi feed pressure is around 6%. *Second*, to implement membrane distillation, the temperature of the feed solution does not have to be too high; feed solution temperature in the range of 50–90 °C can generate high enough water vapor fluxes. The hot feed solution pressure is around atmospheric so that the demands on the membrane and the membrane device are much less severe than in RO. *Third*, often waste heat and low grade heat may be available allowing their use in MD as opposed to costlier electrical energy in RO. *Fourth*, there are many examples where desalination of a hot aqueous solution is needed as for example produced water obtained in oil exploration. RO membranes cannot handle higher temperatures and requires cooling down of the feed solution. The capacity of RO membranes to handle precipitation of scaling salts is also quite limited leading to extensive use of antiscalants. There is a significant possibility that in MD the problem of membrane fouling by scaling salts can be controlled [8].

Membrane fouling is a major concern in most membrane operations. It is no different in MD. Further it is always the hot feed side whose fouling has to be controlled. The sources of fouling of special relevance to MD depend on the feed being treated. In MD-based concentration processes of juices, etc., small amounts of protein present is likely to foul the membrane. In desalination, salt crystals precipitating from the brine on the membrane surface as it is being concentrated and the precipitation of crystals of scaling salts having very low solubility such as $CaSO_4$, $CaCO_3$ are of great concern. There are two ways this problem has been solved. In one approach, specific types of hollow fibers having a particular type of fluorosiloxane coating was employed in rectangular cross-flow modules which prevented scaling of membranes even though there was extensive amount of precipitation of scaling salts. He et al. [9–11] studied desalination in laboratory in the presence of supersaturated solutions of $CaSO_4$, $CaCO_3$ having very high saturation index (SI) values. The water vapor flux remained unaffected during extended periods of operation. The performance of a large pilot plant [8] employing this technology demonstrated its usefulness in large-scale operation.

Guillen-Burrieza et al. [12] studied membrane fouling and damage during intermittent long-term (2010–2013) solar-powered pilot plant-scale AGMD operation for desalination and studied different cleaning strategies to remove the fouling layer and restore the membrane properties. Effective membrane cleaning was demonstrated. This study is important: even if one avoids scaling during operation of the plant, scaling can occur when the plant is shut down. Hickenbottom and Cath [13] had exchanged the flow between the feed channel and the distillate channel or reversed the direction of ΔT between the two channels and achieved considerable control of scaling in batch studies with hypersaline solutions. Lee et al. [14] recommended using dilute solutions of HCl and brine to restore the original performance of membrane after it was used to concentrate artificial seawater by 8 times in the laboratory. Curcio et al. [15] employed a two-step cleaning strategy with an aqueous citric acid solution (20 min)/aqueous NaOH solution (20 min) to restore the transmembrane flux and membrane hydrophobicity. Table 7.1 summarizes results of various studies involving fouling and cleaning.

Table 7.1 Membrane fouling in MD and cleaning methods

Reference MD technique Membrane (pore size) Scale of study	Type of feed and nature of membrane operation	Foulants and effect of fouling	Cleaning method (s)	Effect of cleaning
Guillen-Burrieza et al. [12] AGMD PTFE (0.18 μm) Pilot plant scale Lab scale	Water solution of marine salts at 1 and 35 g/l. Intermittent operation for 3 year lasting for 8 h each day and shut down	Fe, Mg, Al oxides from rusting pipes and NaCl	DI, citric acid, formic acid, sulfuric acid, oxalic/citric acid, EDTA/phosphate detergent	Lower LEP; lower contact angle; higher permeate conductivity; higher flux
Song et al. [8] DCMD hollow fibers of PP (max. pore size, 0.6 μm) with a porous coating of fluorosilicone; Pilot plant scale	City water with added salt for 3 months-8 h/day; brine drained. Trucked-in seawater concentrated continuously to 19% salt	No observed flux reduction except due to increased salt concentration; No increase in permeate salt concentration	Just water wash if needed	No observed effect except contact angle reduced and slight browning of surface
He et al. [9] DCMD PP (maxm. pore size, 0.6 μm) with a porous coating of fluorosilicone; Lab scale	Brine containing 18.3–35.0 mmol/l of Ca++ in the form of $CaSO_4$ 8 h each day	No observed flux reduction; No increase in permeate salt concentration	0.06 M NaCl solution was flushed through the shell side to dissolve the remaining Ca ++ deposits	No observed effect
Lee et al. [14] DCMD PP (max. pore size, 0.6 μm) with a porous coating of fluorosilicone; Lab scale: cascade of four small modules	Artificial sea water concentrated 8 times 8-hr operation every day	Flux reduced considerably as the brine got concentrated	Dilute NaCl solution and 5% HCl solution used to clean the shell side of the membrane device	Flux was restored to 95% of the original flux

(continued)

Table 7.1 (continued)

Reference MD technique Membrane (pore size) Scale of study	Type of feed and nature of membrane operation	Foulants and effect of fouling	Cleaning method (s)	Effect of cleaning
Curcio et al. [15] DCMD PP membrane (0.7, porosity) Lab Scale	Synthetic sea water; humic acid present; Concentrated 4–6 times; Uninterrupted operation for 35 h	$CaCO_3$ crystals deposited; Initial flux reduced by 45%	2-step cleaning; 20 min: pH 4 citric acid and 20 min 0.1 M NaOH solution; each step preceded and followed by DI water washing	Flux completely restored by cleaning
Hickenbottom and Cath [13] DCMD Membrane: PTFE (PP supported) and PP (0.22 μm) Lab scale	Water from great salt lake—150,000 mg/L total dissolved solids. Two times concentrated Regular lab operation and 125-hr operation	Flux reduced by 80%. Sparingly soluble salts precipitated	Flow reversal (exchange feed and distillate flow channels); Temperature reversal (colder feed stream and warmer distillate stream)	Water vapor fluxes restored by the two techniques

Many membrane distillation studies investigate thermal efficiency: the fraction of the brine sensible heat lost that is used to evaporate water; the rest of the heat is lost by conduction to the other side of the membrane. In DCMD, considerable heat is lost by conduction to the distillate; thermal efficiency achieved is generally ~50–60%. Lee et al. [14] achieved a value of ~86% by using a low temperature difference between the hot brine and the cold distillate. In VMD, the value of this thermal efficiency is high approaching close to 100%. Another important metric from an energy aspect is gained output ratio (GOR). From a practical perspective, GOR indicates how many kg of water is evaporated in the MD process per kg of steam supplied to heat the brine. Virtually almost all DCMD studies have made no effort to operate at values of GOR > 1. Lee et al. [14] operated a cascade of DCMD modules and came close to a GOR value of 6.

This chapter will focus on many applications of MD employing primarily the techniques of DCMD, VMD, and AGMD. We will briefly identify at the beginning of the next section various types of applications of MD to solve a variety of problems in desalination and water treatment; then we will provide more information about each category with particular examples.

7.2 Membrane Distillation Applications

The following categories of applications will be covered: Desalination of seawater and brackish water; produced water treatment from oil exploration and coal seam gas production; high temperature DCMD; water treatment in membrane bioreactors and for oily wastewater; treatment of dairy, food and beverage process streams; concentration of acids; mineral recovery; radioactive water treatment. Most recent studies will be identified in general.

7.2.1 Desalination of Seawater and Brackish Water

Trucked-in seawater was concentrated in a hollow fiber module based pilot plant [8] by DCMD using the batch recirculation technique to a salt concentration level of ~20%. The distilled water production rate was 0.62 gpm. There was no salt leakage. There was essentially very limited flux reduction observed till salt concentration increased to around 19% even though precipitates were floating all around due to the high concentration of scaling salts developed as the seawater was being concentrated. The scaling salt concentrations in the form of precipitates were around 10,000 ppm. Using somewhat smaller modules having the same design and the same kind of hollow fibers, Song et al. [7] studied DCMD-based desalination of artificial brines containing 3, 6, 10% salt; they also studied desalination of city water. The salt concentration increase led to a maximum of 10% reduction in the water vapor flux. The modules had 0.28 m^2 membrane surface area [7] compared to 0.66 m^2 in the pilot plant [8] and 119 cm^2 in laboratory studies. As already mentioned, Lee et al. [14] demonstrated achievement of a value of around 6 for the GOR in a multi-staged cascade-based operation with an artificial brine; the theoretical model indicated that GOR values of 10–14 can be achieved had heat losses in the system were avoided by using insulation around the membrane units.

High salinity brines from thermal distillation plants having 70,000 mg/L total dissolved solids (TDS) were treated by MD [16]. The bench-scale study produced high-quality distillate (<10 μS/cm). This approach can reduce the impact of hot concentrated brine discharge into the sea. Minier-Matar et al. [17] carried out pilot-scale tests of treating brines from thermal desalination plants using a variety of MD technologies. High-quality distillate with salt rejection higher than 99.9% was achieved. Hou et al. [18] investigated boron rejection from brines at various pHs and temperatures using PVDF membranes. The boron removal efficiency was >99.8%. The permeate boron level was below 20 μg/L; the permeate boron level was below the maximum permissible level at feed concentrations as high as 750 mg/L. Boubakri et al. [19] studied the effect of operating parameters on boron removal from seawater using a PVDF membrane-based DCMD process; 90% removal was achieved at feed concentration as high as 200 mg/L.

7.2.2 Produced Water Treatment from Oil Exploration and Coal Seam Gas Production

Many millions of barrels of produced water are generated every day as millions of barrels of oil are extracted every day. The ratio can be easily five to seven barrels of water per barrel of oil. Singh et al. [20] investigated concentration of de-oiled produced water by DCMD using rectangular cross-flow modules containing polypropylene (PP) hollow fibers having a nearly superhydrophobic fluorosilicone coating which had a larger pore size than the PP substrate. High-quality permeate water was obtained even when the feed brine was concentrated via batch recirculation to recover 80% water, due to the novel coated membrane and the hollow fiber module design. The flux was reduced by ~20–30%. No special module cleaning was needed. The DCMD treatment of the de-oiled produced water (from Chevron Corp.; obtained after induced gas flotation (IGF) and walnut shell filter treatment (the so-called Post-Wemco water [21]) to remove free oil as much as possible and used in the DCMD investigation) essentially bypassed seven to eight steps (including cooling) leading to RO treatment at around room temperature employed by the conventional OPUS$^{\mathrm{TM}}$ technology. See Fig. 7.2.

Macedonio et al. [22] studied DCMD treatment of oilfield produced water using PVDF and PP membrane-based modules. Salt rejection factor greater than 99% and total carbon rejection higher than 90% were achieved. An economical evaluation was also carried out to assess the feasibility of the DCMD process. With a recovery of 70%, water cost was \$0.72/m^3 at a feed temperature of 50 °C.

A pilot plant study was implemented by Duong et al. [23] to treat RO brine from coal seam gas (CSG) produced water by AGMD in a spiral-wound module. It was discovered that initially at the distillate production rate of 15 L/h, the pilot MD

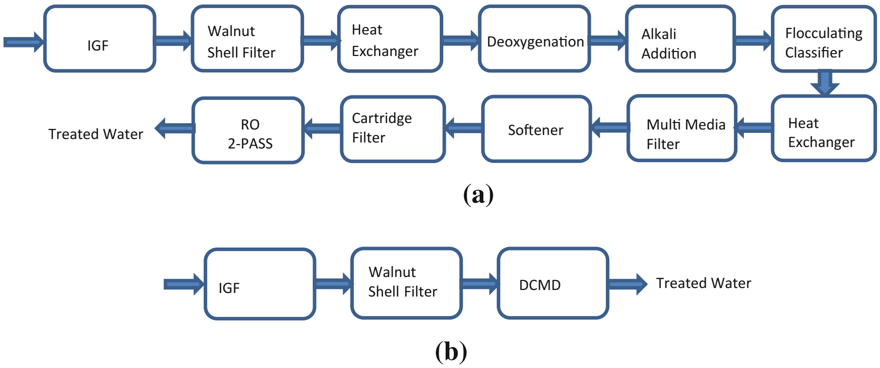

Fig. 7.2 Schematic diagrams showing various steps involved in **a** OPUS$^{\mathrm{TM}}$ technology and **b** DCMD-based technology for hot produced water treatment

system had a GOR value of 4, and the specific thermal energy consumption (STEC) (kWh/m^3) value of the system was 175 kWh/m^3. As the distillate production rate decreased to 10 L/h because of the increased water recovery rate, GOR gradually decreased to 2.5 and STEC value increased to 250 kWh/m^3. Woo et al. [24] studied graphene/PVDF flat sheet membrane for the treatment of RO brine from CSG produced water by AGMD. Membranes having a range of graphene loadings in the range of 0.1–2.0 wt% (w.r.t. to PVDF) were prepared via phase inversion. Surface characterization indicated high porosity (>0.78), mean pore size <0.11 μm, and a high liquid entry pressure (43.6 atm). AGMD test results yielded a high water vapor flux of 20 L/m^2-h and a salt rejection of 99.99% at a graphene loading of 0.5 wt% which was found to be optimal.

7.2.3 High Temperature DCMD

Singh and Sirkar [25] explored DCMD for treating simulated brine coming out of the steam assisted gravity drainage (SAGD) process during recovery of heavy oil and bitumen from Canadian oil shales. They employed microporous polytetrafluoroethylene (PTFE) flat membranes of 0.03 μm pore size and 23 μm thickness as well as PTFE hollow fibers (of pore size 0.24 μm; Singh and Sirkar [26]) to successfully recover water from simulated SAGD produced water at 2–3 atm and temperature in the range of 100–128 °C without any salt leakage. For the flat membranes the water vapor flux could be as high as 195 kg/m^2-h at 128 °C. For the hollow fibers, the water vapor flux was as high as 115 kg/m^2-h at 118 °C. The remarkable enhancement in flux is primarily due to the exponentially increasing vapor pressure with increasing temperature.

The paper by Elsayed et al. [27] examined membrane distillation (MD) as an integral part of water treatment for steam assisted gravity drainage (SAGD) process during recovery of heavy oil and bitumen. The two primary waste water streams generated during SAGD process were treated by MD by taking the advantages of relatively high temperature of two waste water streams. Several design configurations and 33 scenarios were proposed and evaluated to assess the technical and economic viability of including direct contact membrane distillation as a process in water-management systems for SAGD. This paper assessed the technical and economic viability of MD as a process in water-management systems for SAGD. It was found that the costs for the various scenarios range from \$0.30 to \$4.47/m^3 of permeate depending on the characteristics of the wastewater, the desired recovery, and the availability of heat sources.

7.2.4 Water Treatment: Bioreactors and Oily Wastewaters

Phattaranawik et al. [28] introduced the water treatment process known as membrane distillation bioreactor (MDBR). This process integrates a conventional wastewater bioreactor, e.g., an activated sludge treatment device, with membrane distillation. Due to the basic nature of the MD process, very high quality treated water is obtained with TOC levels below 1 ppm and negligible salts. The MDBR uses thermophilic bacteria at ~50 °C to treat wastewater. Water vapor fluxes in the range of 2–5 kg/m^2-h are obtained in a sustained way over extended periods.

Goh et al. (2015) [29] reviewed the membrane distillation bioreactor (MDBR) for wastewater reclamation systems. MDBR is comparable to the MBR–RO as a flux of 10 L/m^2-h was able to be achieved in short term study (MBR stands for membrane bioreactor). The permeate quality for MDBR and MBR–RO were similar in most of the studies except for ammonium ion concentration in the water from MDBR which need to be reduced by further treatment for boiler water and cooling water applications.

Kim et al. [30] investigated direct contact membrane distillation combined with an anaerobic moving bed biofilm reactor (AMBBR) for treating municipal wastewater. During long-term distillation with the PVDF membrane, total phosphorus was completely rejected and >98% rejection of dissolved organic carbon was also achieved. Zhang et al. [31] explored the possibilities of sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD). At least 90% feed water recovery was attained with only trace amounts of oil and salts. Acetic acid in permeate could be retained for further reuse as a chemical additive during the production of crude oil.

Employing DCMD, Wijekoon et al. [32] studied the rejection and fate of trace organic compounds (TrOCs) present during water and wastewater treatment. Twenty-nine compounds including pharmaceuticals, steroid hormones, industrial chemicals, pesticides, phytoestrogens, UV-filters were studied for their presence in permeate from the DCMD process. The rejection, fate and transport of these TrOCs depend on their volatility and to a lesser extent their hydrophobicity. Those compounds whose pK_H is larger than 9 could be classified as nonvolatile and were well removed by DCMD. A few compounds with moderate volatility ($pK_H < 9$) encountered limited rejection of around 50–75%. Hydrophilic compounds with negligible volatility were concentrated in the feed whereas hydrophobic compounds possessing moderate volatility were lost by evaporation (thus contaminating permeate) or by adsorption. When the investigators employed MDBR, near complete removal (>95%) was achieved for every one of the 29 compounds studied regardless of their hydrophobicity, volatility and persistency. Such a result is supported by the general conclusions of Goh et al. [29].

7.2.5 *Treatment of Process Streams from Dairy, Food, Beverage Industries and Animal Husbandry*

The MD technique has been explored for concentration of orange juice, milk, aqueous solution of glucose, gelatin, ethanol among others. These investigations were initiated as early as 1987. More volatile organic species like ethanol were concentrated in permeate. A permeate containing 50% ethanol was achieved by using polytetrafluorethylene membranes. The references to these earlier research results are provided in Sirkar [1]. Here we identify a few recent investigations. For example, Kezia et al. [33] employed DCMD to investigate concentration of the waste effluent from salty whey, a byproduct of cheese making. The effect of trace protein in the feed, cross-flow velocity and feed acidity were then examined using three flat sheet PTFE membranes. A range of 37–83% of water recovery was achieved from less than 10 wt% solids to 30 wt% solids feed stream. Trace protein if not removed will foul the membrane strongly. The cleaning-in-place (CIP) of the membrane was conducted by circulating solutions in an acid–base–acid cleaning cycle. The cleaning agent consisted of 30% HNO_3 and 30% H_3PO_4 at pH 3 whereas the concentrated alkaline cleaning agent was made of 10% NaOH and 10% EDTA at pH 11.

Kiai et al. [34] studied application of membrane distillation technology in the treatment of table olive wastewaters (TOW) for phenolic compounds concentration and high-quality water production. Three PTFE membranes supported by polypropylene net were investigated. Separation factors higher than 99.5% was achieved after 4 h of TOW processing and concentration factor was reached up to 2.2. Purwasasmita et al. [35] investigated MD for beer dealcoholization using vacuum membrane distillation method with non-porous membrane without diffusion of maltose and glycerol through the membrane pores. The membrane flux and ethanol concentration in permeate were 0.15–0.76 L/m^{2}h and 3.66–4.64 vol%, respectively.

Zarebska et al. [36] studied fouling mitigation of PP and PTFE membranes in membrane distillation processes during ammonia stripping from pig manure. Using PVDF membrane-based MF or UF as a pretreatment prior to MD increased the ammonia mass transfer coefficient twofold for the PTFE membrane and fourfold for the PP membrane. For membranes fouled with model manure solution, Novadan agents were the most successful cleaning agents studied in removing proteins and carbohydrates from the PTFE membrane as it increased the contact angle and restored the membrane hydrophobicity. Kim et al. [37] investigated DCMD process to remove water from anaerobic digestate as feed. This feed was obtained from anaerobic digestion of livestock wastewater having a high concentration of suspended solids, chemical oxygen demand, and total nitrogen. In short-term experiments, no fouling occurred; experiments running or 72 h showed very high flux decline.

7.2.6 Concentration of Acids

Tomaszewska et al. [38] investigated concentration of various acids by the DCMD technique. For the nonvolatile acids, sulfuric and phosphoric, permeate obtained was acid-free. Sulfuric acid could be concentrated up to 63%. However, for slightly volatile acids, e.g., hydrochloric acid, and nitric acid, the permeate concentration of the volatile acids increased with the feed concentration. These results are similar to those obtained in 1987 by Kimura et al. (see [1]) who had concluded that condensate solute concentrations became equal to those of the feed when the feed solute concentrations were higher than 1 mol/L. The removal of the volatile hydrochloric acid from a reaction mixture through a membrane distillation process into water to produce a dilute acid solution was demonstrated by Tomaszewska and Lapin [39]; HCl was produced during the production of potassium bisulfate via the reaction between KCl and H_2SO_4. This reaction was the first step toward the production of the fertilizer potassium sulfate.

Feng et al. [40] studied the concentration of synthetic titanium white acid solution containing $FeSO_4$ using laboratory-made PVDF hollow fiber membranes in DCMD. The feed acid was commonly a waste seen in the industrial production of titanium dioxide or Titania (TiO_2), which is an important compound used in various fields, such as plastics and pharmaceuticals. Crystals of $FeSO_4$ were found homogeneously distributed on the outer surface of the hollow fibers while treating $H_2SO_4/FeSO_4$ solution. The salt rejections were maintained at a high level throughout the DCMD process before cleaning by rinsing the module with 2–5 wt % HCl solutions.

7.2.7 Membrane Distillation in Biorefineries

Zhang et al. [41] investigated simultaneous concentration and detoxification of lignocellulosic hydrolyzates by VMD coupled with adsorption of acetic acid by a weakly basic resin Amberlite IRA67. The sugar concentration obtained after hydrolysis is low. It has to be increased for subsequent fermentation. After acid hydrolysis or thermochemical treatment, there are also a number of byproducts such as furans and acetic acid obtained due to the complex nature of the feedstock. Hollow fiber-based VMD was applied to concentrate the hydrolysate; further adsorption of acetic acid using Amberlite resin or activated carbon was applied on the vacuum side to maintain a low partial pressure of acetic acid for its efficient removal from the hydrolysate. The ethanol production of hydrolyzates concentrated and detoxified were approximately 10-fold greater than from those utilizing untreated hydrolyzates.

7.2.8 Mineral Recovery

Quist-Jensen et al. [42] utilized membrane distillation and membrane crystallization (MCr) for the treatment of industrial wastewater containing high amounts of sodium sulfate. Stable performance in more than 90 h with no decline in transmembrane flux was observed, despite the very high scaling potential of components, such as silica, calcium, and magnesium in the untreated industrial wastewater. Sodium sulfate has been recovered as a high-quality product in terms of narrow size distribution, low coefficient of variation, constant growth rate, and low incorporation of impurities. The potential of recycling salts or other valuable compounds from industrial waste minimizes the future possibility of mineral depletion.

Hickenbottom and Cath [13] employed DCMD to concentrate water from the Great Salt Lake (>150,000 mg/L TDS) as the feed stream to twice its original concentration. This approach was compared to natural evaporation ponds; using extrapolation based on observed fluxes it was concluded that the membrane surface area required would be more than two orders of magnitude smaller than that of an evaporation pond. There was an extraordinary amount (80%) of flux reduction during the concentration in this lab scale study due to membrane surface scaling which was solved by a novel scale-mitigation technique based on flow reversal or temperature reversal.

7.2.9 Radioactive Water Treatment

Khayet et al. [43] proposed DCMD for low- and medium-level radioactive waste liquid processing and recover water. Distilled water, non-active solutions of inorganic salts, and solutions with admixtures of radionuclides and simulated and real radioactive waste samples were used as feeds in both laboratory and pilot plant experiments. The real radioactive waste sample of ^{51}Cr, ^{60}Co, ^{134}Cs, and ^{137}Cs was concentrated about 10 times from specific activity of about 1800–17.8 × 10^3 Bq/L in laboratory shell-and-tube capillary Euro-Sep module. Liu and Wang [44] used DCMD to treat low level radioactive wastewater (LLRW). Almost all Cs(+), Sr(2+) and Co(2+) could be separated from the recovered water from a feed solution containing $NaNO_3$ at as high a level as 200 g/L. Khayet [45] studied treatment of radioactive waste water solutions by DCMD using polymeric membranes of polysulfone and polyethersulfone. These membranes were surface-modified by incorporating surface modifying macromolecules (SMMs) during the phase inversion process of making membranes and making their top surfaces exposed to the feed solution hydrophobic. Model solutions studied contained radioisotopes commonly present in radioactive liquid wastes, e.g., Co-60, Cs-137, Sr-85. The permeate obtained had radioactive activity on the level of the natural background. The performances of the surface-modified membranes were similar to that of a commercial membrane TF200 (Gelman). A review of examples of radioactive decontamination of water by membrane processes by Rana et al. [46] provides a window into the use of membrane distillation-based studies. Table 7.2 provides a summary of different membrane distillation case studies.

Table 7.2 Summary of different membrane distillation case studies

Reference	MD process and scale of study	Membranes/modules	Type of feed	Results
Desalination of seawater and brackish water				
Song et al. [8]	DCMD (Pilot scale)	PP hollow fibers with a porous coating of fluorosilicone	City water with added salt up to ∼20% conc.; trucked-in seawater	Distilled water production rate 0.62 gpm; no salt leakage
Song et al. [7]	DCMD (lab scale)	PP hollow fibers as in [8]	City water; artificial brines containing 3, 6, 10% salt;	Small flux reduction for 10% salt conc.; no pore wetting.
Adham et al. [16]	DCMD (bench scale)	PTFE	Brines from thermal distillation plants; 70,000 mg/L TDS	Produced high-quality distillate (<10 μS/cm)
Minier-Matar et al. [17]	VMD & AGMD (pilot scale)	PTFE	Brines from thermal desalination plants	High-quality distillate with salt rejection higher than 99.9%
Hou et al. [18]	DCMD (lab scale)	PVDF membranes	Brines at various pH	The boron removal efficiency was >99.8%; permeate boron level was below 20 μg/L
Boubakri et al. [19]	DCMD	PVDF membrane	Sea water	90% removal was achieved at feed concentration as high as 200 mg/L
Produced water treatment from oil exploration and coal seam gas production				
Singh et al. [20]	DCMD (Lab Scale)	PP hollow fibers as in [8]	De-oiled produced water from Chevron Corp.	High-quality permeate when brine was concentrated to recover 80% water
Macedonio et al. [22]	DCMD (lab scale)	PVDF and PP membrane	Oilfield produced water	Salt rejection factor >99% and total carbon rejection >90%, with a recovery of 70%, water cost was $\$0.72/m^3$ at feed temperature 50 °C

(continued)

Table 7.2 (continued)

Reference	MD process and scale of study	Membranes/modules	Type of feed	Results
Duong et al. [23]	AGMD (Lab& Pilot Scale)	Polyethylene	RO brine from coal seam gas (CSG) produced water	At the distillate production rate of 15 L/h, the pilot MD system had a GOR of 4, and the specific thermal energy consumption 175 kWh/m^3
Woo et al. 2016 [24]	AGMD (Lab Scale)	Graphene/PVDF	RO brine from CSG produced water	High water vapor flux and salt rejection of 20.5 L/m^2-h and 99.99% respectively
Singh and Sirkar [25]	DCMD (Lab Scale)	PTFE flat membrane	Simulated SAGD produced water	Water vapor flux, 195 kg/m^2-h at 128 °C
Singh and Sirkar [26])	DCMD (Lab Scale)	PTFE Hollow Fibers	Simulated SAGD produced water	Water vapor flux 115 kg/m^2-h at 118 °C
Elsayed et al. [27]	MD	Modeling paper	SAGD produced water	Costs range from \$0.30–\$4.47/m^3 of permeate
Water treatment: Bioreactors and oily wastewaters				
Phattaranawik et al. [28]	MD Bioreactor	PVDF	Wastewater having thermophilic bacteria	Water vapor fluxes in the range of 2–5 kg/m^2-h
Goh et al. [29]	MD Bioreactor	Review paper-PVDF and PTFE	Wastewater	Flux of 10 L/m^2-h achieved in short term study
Kim et al. [30]	DCMD	PVDF	Municipal wastewater	Phosphorus was completely rejected; >98% rejection of dissolved organic carbon
Zhang et al. [31]	Forward osmosis-MD	PVDF	Oily wastewater	90% feed water recovery was attained with only trace amounts of oil and salts
Wijekoon et al. [32]	DCMD (lab scale)	PTFE	Wastewater	Compounds whose pK_H is >9 were removed by DCMD; For moderate volatility (pK_H <9), rejection of 50–75%

(continued)

Table 7.2 (continued)

Reference	MD process and scale of study	Membranes/modules	Type of feed	Results
Process streams from dairy, food, beverage industries and animal husbandry				
Kezia et al. [33]	DCMD	PTFE membrane	Waste effluent from salty whey	37–83% of water recovery from less than 10 wt% solids to 30 wt% solids feed stream
Kiai et al. [34]	MD (Lab)	PTFE membrane	Table olive wastewaters (TOW)	Separation factor >99.5%; conc. factor was up to 2.2
Purwasasmita et al. [35]	VMD (Lab Scale)	Polyamide	beer	Flux and ethanol concentration in permeate were 0.15–0.76 LMH and 3.66–4.64%-vol. respectively
Zarebska et al. [36]	MD (Lab)	PP and PTFE membranes	Pig manure	Ammonia recovered from animal waste
Kim et al. [37]	DCMD (Lab Scale)	PVDF	Anaerobic digestate	No fouling occurred; experiments running for 72 h showed very high flux decline
Concentration of acids				
Tomaszewska et al. [38]	DCMD (lab scale)	PTFE and PP	Acid streams	Sulfuric acid concentrated up to 63%. For slightly volatile acids, the permeate conc. of the volatile acids increased with the feed concentration
Tomaszewska et al. [39]	MD Process	Accurel PP capillary membrane	HCl producing reaction mixtures	HCl was produced during production of potassium bisulfate.
Feng et al. [40]	DCMD (Lab scale)	PVDF membrane	Synthetic titanium white acid solution containing $FeSO_4$	Crystals of $FeSO_4$ were found homogeneously distributed on the outer surface of the fibers

(continued)

Table 7.2 (continued)

Reference	MD process and scale of study	Membranes/modules	Type of feed	Results
Mineral recovery				
Quist-Jensen et al. [42]	DCMD (lab scale)	PP hollow fibers	Industrial wastewater having high amounts of sodium sulfate	Sodium sulfate has been recovered as a high-quality product in terms of narrow size distribution, and constant growth rate
Hickenbottom and Cath [13]	DCMD	PTFE and PP	Great Salt Lake (GSL) (>150,000 mg/L TDS)	DCMD was effective in concentrating GSL water to greater than 350,000 mg/L
Radioactive water treatment				
Khayet et al. [43]	DCMD (lab and pilot scale)	PP, PVDF, and PTFE	Distilled water, non-active solutions of inorganic salts and solutions with admixtures of radionuclides and simulated and real radioactive waste	The real radioactive waste sample of ^{51}Cr, ^{60}Co, ^{134}Cs and ^{137}Cs was concentrated about 10 times from specific activity of about 1800 to 17.8 × 10^3 Bq/L
Liu and Wang [44]	DCMD (cale)	PVDF	Low level radioactive wastewater (LLRW)	Almost all Cs(+), Sr(2+) and Co(2+) could be separated from the recovered water from a feed solution containing $NaNO_3$ at as high a level as 200 g/L
Khayet [45]	DCMD	Polysulfone and polyethersulfone	Radioactive waste water solutions	Permeate obtained had radioactive activity on the level of the natural background

7.3 Concluding Remarks

Membrane Distillation (MD) is a promising technology in desalination and water treatment. In this chapter, a variety of applications of MD employing primarily the techniques of DCMD, VMD, and AGMD are presented. The potential research areas in MD which require further investigation are as follows. (1) Most MD studies involve laboratory scale experiments. Large-scale MD studies covering industrial applications mentioned above are areas of potential research. (2) Membrane fouling is a major concern in most membrane operations in almost all industrial fields. It has been proven that using suitable membranes and membrane cell/module design and operating conditions, membrane fouling due to the presence of scaling salts will have minimal effect on MD performance. This is a major advantage in MD compared with RO and other conventional desalination methods. (3) Energy consumption analysis needs further attention as limited investigations have been carried out. Progress in these three areas will facilitate movement of industries further towards a more sustainable MD development.

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Chapter 8
Zero Liquid Discharge in Desalination

Francesca Macedonio and Enrico Drioli

Abstract Global water stress, raw material depletion, environmental pollution, energy production, and consumption are already severe problems that our modern society have to solve and overcome for maintaining and increasing the quality of our life. Membrane engineering with its various operations is one of the disciplines more involved in the technological innovations necessary to face these strongly interconnected problems. In this work, the most interesting aspects of membrane engineering in water desalination are identified, not only for the production of freshwater but also for the production of energy and for the recovery of metals from the concentrated waste streams of the desalination plants. In particular, the potentialities of integrated membrane-based desalination processes with membrane distillation (MD)/membrane crystallization (MCr)/pressure-retarded osmosis/reverse electrodialysis units are described. Desalination processes designed in this way could become *closed systems*, exploiting seawater in order to approach *zero liquid discharge* (ZLD), or near ZLD, and *total raw materials utilization*.

Keywords Integrated membrane-based desalination system · Energy production · Blue energy · Membrane contactors · Membrane desalination costs

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8.1 Introduction

Energy consumption, raw materials deployment, water scarcity, and environmental protection are the major challenges affecting every continent around the world. According to the latest report of the World Health Organization and UNICEF "Progress on Drinking Water and Sanitation—2014 update" [1], in 2012, 748 million people still lack access to improved sources of drinking water and more than one-third of the global population—some 2.5 billion people—do not use an improved sanitation facility. Three years of research from Aarhus University in Denmark, Vermont Law School and CNA Corporation in the US published in 2014 show that by 2020 about 30–40% of the world will have water scarcity and by the year 2040 there will not be enough drinking water in the world to quench the thirst of the world population. In the last decades, energy consumption has also grown rapidly and is projected to increase further in the following years [2] (Fig. 8.1). Moreover, water and energy demand are strongly interconnected: taking into account that in many countries, electricity is the biggest source of water consumption because the power plants need cooling cycles in order to function, it has been estimated that it will be impossible to continue to produce electricity in this way and meet the water demand by 2040.

Mineral deficiency is also becoming quite common all over the world in the last years. For example, the demand for lithium has already doubled over the past decade and it is expected to more than double over the next 10 years. In the case of uranium, the demand (as energy source) has already exceeded the global production and it is projected to increase from 61,500 tons in 1997 to 75,000 tons in 2020 [3]. It has been also estimated that other compounds, such as antimony, indium, silver,

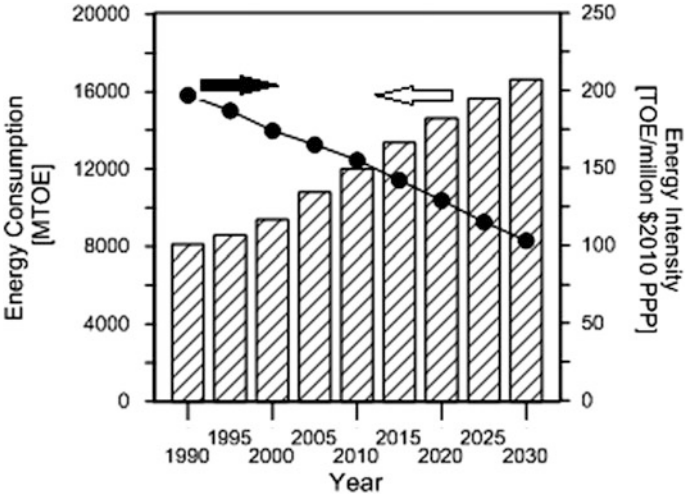

Fig. 8.1 Outlook of energy consumption *left axis* and energy intensity *right axis* (from [2])

and zinc, will leave within the next 46 years if the world continues to consume at today's rate and within 30 years if demand will grow (Table 8.1).

Membrane engineering with its various operations is one of the disciplines most involved in the technological innovations necessary to face the strongly interconnected problems of water shortage, increasing energy consumptions, mineral depletion, and environmental protection. In the last years, the impact of membrane operations in various areas has grown fast. Seawater and brackish water desalination, industrial water reuse, wastewater treatment, gases separations, membrane bioreactors, hybrid artificial organs, and agro-industry (such as dairy industry, juices and wine productions, etc.) are typical examples of membrane engineering success. The motivation for this success is in large part related to their basic properties in terms of energy consumption, low environmental impacts, no use of chemicals, easy automatization, etc. All these aspects are very well related to the strategy of Process Intensification (PI). The latter entails to (1) maximize the effectiveness of intra- and intermolecular events; (2) give each molecule the same processing experience; (3) optimize the driving forces at every scale and maximize the specific surface area to which these forces apply; and (4) maximize the synergistic effects from partial processes [5, 6]. Membrane engineering is a technology

Table 8.1 Raw material depletion: one problem of today and tomorrow. Adapted from [4]

	How many years left if the world consumes at today's rate	How many years left if the world consumes at half the US consumption rate	If demand grows (some resources will be exhausted more quickly if predicted new technologies appear and the population grows) (years)
Antimony (drugs)	30	13	15–20
Indium (LCDs)	13	4	5–10
Platinum (jewelery, catalysts, fuel cells for cars)	360	42	15
Silver (jewelery, catalytic converters)	29	9	15–20
Tantalum (cellphones, camera lenses)	116	20	20–30
Uranium (weapons, power station)	59	19	30–40
Zinc (galvanizing)	46	34	20–30

in which all the requirements of PI can be realized due to its intrinsic characteristics of advanced molecular separation, improved efficiency, ease of operation and scale-up, and aptitude to integrate different but complementary membrane operations [6]. Membrane engineering can represent a problem-solver with intercorrelated solutions. In the last years, for example, membrane operations have been already assigned a key role in water reclamation schemes that are aimed at higher water quality reuse applications (i.e., reverse osmosis is considered one of the most promising technologies for desalting salty waters). At present, redesign of important industrial production cycles (such as desalination) by combining various membrane operations (such as the traditional membrane MF, UF, NF, RO separation operations with the new membrane MD, MCr, PRO, RED systems) can realize highly integrated membrane processes offering comprehensive prospects to the solution of future water, energy, and raw materials demands.

The present chapter will highlight the use of membrane operations for materials extraction, water and energy production from the sea and in particular from the brine streams of the desalination plants thus approaching the concept of "zero-liquid-discharge" and "total raw materials utilization" [7–10]. The latter are strategies aiming to process the waste streams of a process in order (i) to recover as much as possible the valuable components contained in those streams and (ii) to minimize disposal problem.

8.2 Desalination

Water is defined to be "fresh" when it contains less than 500 ppm of total dissolved salts (TDS). However, many countries have higher upper salinity limits for freshwater (e.g., 1000 or 3000 ppm) [11]. For example, the World Health Organization (WHO) and the Gulf Drinking Water standards recommend a drinking water standard of 1000 mg/L TDS. Australia and California [11] have drinking water standard of 1000 mg/L TDS, too. The state of Utah has a TDS limit of 2000 mg/L, while Florida has a standard of 500 mg/L TDS [11]. Desalination refers to any of several processes that remove excess salts and other minerals from water. Water is desalinated in order to be converted to freshwater suitable for human consumption or irrigation in regions where the availability of freshwater is limited. These processes can also produce different types of salts as by-products. The principal desalination technologies can be classified by their separation mechanism into thermal and membrane desalination methods. Thermal desalination processes (such as multistage flash (MSF), multi-effect distillation (MED), vapor compression (VC)) separate salt from water by evaporation and condensation, whereas membrane processes (such as reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED)) use semi-permeable membranes and pressure or an electrical field to separate salts from water.

Thermal desalination has been used for hundreds of years. At present RO is the leading desalination technology accounting for around 60% of all desalination plants [12].

The key to widespread interest and implementation of seawater RO plants has been a significant reduction in capital and operation/maintenance costs over the past 30 years. Several factors have helped in reducing RO energy consumption and costs, including improvements in membrane materials and technology (higher flux, higher salt rejection, lower hydrostatic pressure required, lower materials cost) and the use of pressure recovery devices. RO has also become less expensive than thermal processes, which require an electricity consumption 10 times higher [13, 14].

Presently, the total global desalination capacity is around 66.4 million m^3/day [15]. Schiermeier [16] reports that in 2016 desalination is projected to exceed 116 billion m^3/day, twice the rate of global water production by desalination in 2008.

Energy consumption, brine disposal, air pollutants, and greenhouse gases emissions represent the crucial factors of desalination. These are the aspects to act on for the improvement of desalination process:

- current state-of-the art seawater RO desalination (SWRO) plants consume between 3 and 4 kWh/m^3 (due to the need for extensive pretreatment and posttreatment). A recent requirement is to aim for a consumption of 1.5 kWh/m^3 by 2030, not far from the theoretical inferior limit that Elimelech [17] postulates at 1.06 kWh/m^3 for seawater at 35,000 ppm salt and at a typical recovery of 50%.
- For what concerns emissions of SWRO plants, these are between 1.4 and 1.8 kg CO_2 per cubic meter of produced water [10].
- Regarding SWRO brines, their disposal raises serious environmental risks due to their high salinity (about twice that of seawater) and the presence of chemicals (such as antiscalants, coagulants, surfactants, alkaline and acid solutions, metal-chelating agents) used in pretreatment or as cleaning chemicals.

Until now, the measures adopted to reduce energy consumption and gas emissions are the recourse to renewable energy sources. On the other hand, the expedients usually utilized for minimizing the impact of high-salinity brines are either dilution of high-salinity brines with other waste streams (such as power plant cooling water) or utilization of efficient diffuser systems or an accurate choice of the discharge zone with favorable hydrodynamics for the rapid dissipation of the salinity load.

For what concerns the energy consumption, taking into account that

(i) a real desalination plant is finite in size and does not operate as a reversible thermodynamic process;
(ii) more than 1 kWh/m^3 of energy is consumed by the intake, pretreatment, posttreatment, and brine discharge stages of the desalination plant [18]; and

(iii) a SWRO pilot-scale desalination system working at 50% recovery has been recently demonstrated [17] to work with an energy consumption of 1.8 kWh/m^3, energy demand for seawater desalination is only 25% higher than the practical minimum energy [10]. Therefore, future plants should focus on SWRO pretreatment and posttreatment stages to improve energy efficiency and brine disposal issues.

Advances in membrane technology can reduce the need for pretreatment through the development of (i) fouling resistant membranes with tailored surface properties, (ii) membrane modules with improved hydrodynamic mixing, (iii) oxidant-resistant membranes, and (iv) the widespread replacement of conventional with membrane pretreatment. As a matter of fact, the latter uses less chemicals and has slower fouling rate; thus, the cleaning frequency and the use of chemicals are reduced compared to conventional seawater pretreatment. Development of innovative and energy-efficient membrane-based desalination technologies (such as MD, MCr, pressure-retarded osmosis (PRO) and reverse electrodialysis (RED)) can reduce also energy consumption and the need for posttreatment. In particular, (i) MD and MCr can be utilized for producing solid materials of high-quality and controlled properties (as specific polymorph of salts), and (ii) pressure-retarded osmosis and reverse electrodialysis can be used to generate energy from RO brine.

Therefore, the redesign of desalination process by combining various membrane operations is an attractive opportunity because of the synergistic effects that can be attained. The overall concept introduced can be summarized as follows: desalination systems could became processes for water/energy/raw material production if they will adopt

(i) membrane operations as RO pretreatment instead of conventional pretreatment in order to minimize membrane fouling and therefore reduce the operating costs,
(ii) MCr and/or MD units as RO posttreatment for the recovery of various chemicals present in the NF and/or RO brine and in order to reduce brine disposal problem and increase water recovery factor, and
(iii) PRO and/or RED for energy production from RO brine.

Integrated membrane-based processes designed in that way could become a closed system, exploiting seawater in order to approach ZLD, or near ZLD, and "total raw materials utilization."

In the following sections, membrane operations for minerals and energy production from the sea will be described.

8.3 Membrane Contactors in Water Treatment and Water Purification

Membrane contactors (MCs) are systems utilizing a hydrophobic membrane with appropriate pore structure as a fixed interface between two different phases without dispersing one phase into another. In these processes the membrane does not act as a selective barrier but rather sustains the interfaces. The separation process is based on the principles of phase equilibrium.

With respect to conventional membrane systems, MCs have some important advantages such as high interfacial area per volume unit, low operating temperatures and pressure, high rejection, modular design, easy scale-up, less membrane fouling, and low sensitivity to concentration polarization phenomenon. Drawbacks are related to the presence of an additional mass transport resistance (the membrane itself) and to the rather limited range of the operating pressures below the breakthrough threshold. The performance of MCs strongly depends on the properties of the membranes used. In general, a high hydrophobicity (for aqueous applications) is required to prevent wetting and mixing between the different phases in contact; elevated permeability leads to high fluxes; high chemical and thermal stability are necessary to improve the membrane resistance to chemical attack and its resistance to degradation and decomposition.

MD and MCr are two examples of MCs that can be used for mitigating the impact of concentrates on the environment and for the recovery of the valuable contained components. In particular:

1. in *MD,* one side (feed side) of a hydrophobic membrane is brought into contact with a heated, aqueous feed solution. The hydrophobic nature of the membrane prevents penetration of the aqueous solution into the pores, resulting in a vapor–liquid interface at each pore entrance. Here, volatile compounds evaporate, diffuse, and/or convect across the pores, and are condensed on the opposite side (permeate) of the system (Fig. 8.2). The driving force of the process is linked to the vapor pressure gradient between the two membrane sides.
2. *Membrane crystallization (MCr)* is conceived as an alternative technology for producing crystals and pure water from supersaturated solutions; the use of the MD technique in the concentration of a solution by solvent removal in the vapor phase is utilized in this application (Fig. 8.3).

The main advantages of MD and Mr are as follows:

(I) Intrinsically less susceptible to fouling compared to pressure-driven membrane operations. This is because (a) the pores are relatively large compared to RO/UF pores, (b) the process liquid cannot wet the membrane; therefore, fouling layers can be deposited only on the membrane surface but not in the membrane pores, and (c) due to the low operating pressure of the process, the deposition of aggregates on the membrane surface would be less compact and only slightly affect the transport resistance.

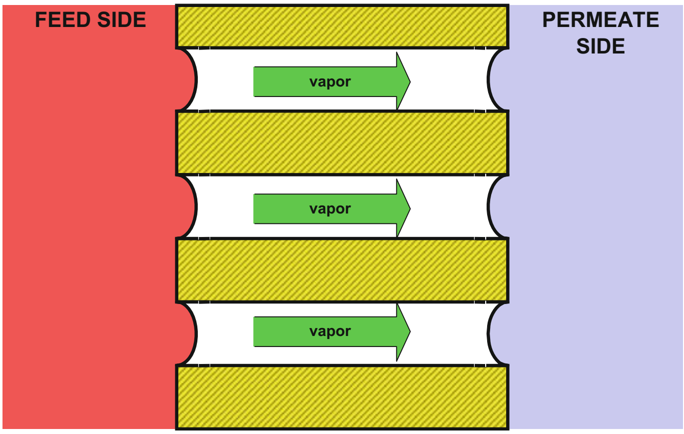

Fig. 8.2 Membrane distillation process

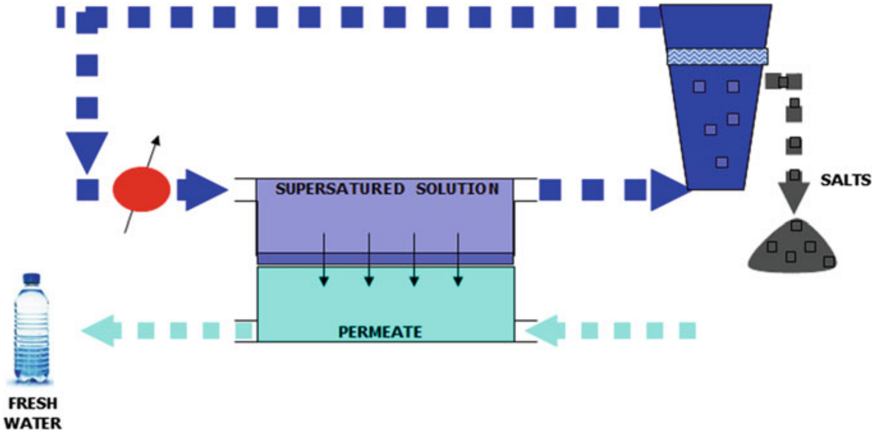

Fig. 8.3 Membrane crystallizer strategy

(ii) Theoretically, 100% impenetrable with respect to nonvolatile components such as macromolecules, colloidal species, and ions. This latter aspect will help both in producing high-quality water and in reducing the RO permeate posttreatment necessary for bringing TDS, boron, and chloride content within the Who's recommended standards. As a matter of fact, in particular regarding boron and chloride concentration in the RO desalinated water, reducing their presence to levels that crops can tolerate necessitates either the chemical treatment of RO permeate or the development of thin-film composite membranes with higher selectivity. The latter, however, due to the separation mechanism of composite membranes, will substantially reduce the membrane permeability and increase energy consumption. MD allows overcoming this problem because the nature of the driving force and the hydro-repellent character of the membrane allows the theoretically complete rejection of nonvolatile components.

(iii) Moreover, both MD and membrane crystallization are inherently less prone to concentration polarization phenomena with respect to membrane-based desalination methods. Therefore, higher recovery factor with respect to RO can be achieved thus reducing the environmental impact of the discharged brine.

Furthermore, MCr is able to promote crystals nucleation and growth in a well-controlled pathway, starting from undersaturated solutions. In a membrane crystallizer the membrane matrix acts as a selective gate for solvent evaporation, modulating the final degree and the rate for the generation of the supersaturation. Hence, the possibility to act on the transmembrane flow rate, by changing the driving force of the process, allows to modulate the final properties of the crystals produced both in terms of structure (polymorphism) and morphology (habit, shape, size, and size distribution). The experimental evidences that can be found in several published articles [19–21] validate the effectiveness of Mr as an advanced method for performing well-behaved crystallization processes.

The studies carried out by Drily and coworkers [22–25] showed that the introduction of a MCr unit on NF and RO retentate streams of an integrated membrane-based desalination system constituted by MF/NF/RO increases plant recovery factor so much to reach 92.4%. Moreover, it has been experimentally shown that the presence of organic compound (i.e., humic acid) in the retentate inhibits crystals growth rate [26]. This proved the necessity to optimize the NF/RO pretreatment steps, in order not only to reduce the NF/RO membrane fouling but also to control the crystallization kinetics that are linked with the nature and the amount of the foreign species existing in the highly concentrated brines emerging from the NF and RO stages.

In some studies on MCr [27] a rapid decrease in trans-membrane flux has been observed due to crystal deposition on the membrane which reduced the membrane permeability. This problem can be minimized through a right design of the process and a proper control of the operative conditions. With respect to the best control of operative conditions, temperature polarization is an important factor depressing the driving force and hereby the process performance. Ali et al. [26] explored the effect of temperature polarization on MD performance by means of a specially designed cell. In particular, a cell with sixteen sensors located at specific locations within its body was built to measure the bulk and membrane surface temperatures on both feed and permeate sides. They found that temperature polarization phenomenon decreases with increasing the feed flow rate, and decreasing the feed inlet temperature and concentration. Moreover, they proved that solution concentration has very less role in flux reduction as compared to thermal polarization at low feed concentration, whereas the flux reduction due to concentration becomes important at high feed concentration where a coupling of heat and mass transfer exists.

Finally, the additional advantage of MD and MCr of low working temperature provides the possibilities to utilize waste heat or other sustainable energy resources (such as geothermal or solar energy).

In the MEDINA project, a work program aimed at improving design and operation practices of the current membrane-based desalination plants was already developed [28]. Project team tried to solve or, at least, to decrease some critical issues of sea and brackish water desalination systems such as improvement of water quality, enhancement of recovery factor, reduction of water cost, and minimization of brine disposal problem. For solving and/or alleviating these problems, an approach based on the integration of different operations in reverse osmosis (RO) pretreatment and posttreatment stages was proposed and studied. In particular, MCr was studied as technology for improving the productivity of desalination systems, recovering some of the valuable ions present in the highly concentrated streams of the desalination plants and reducing their environmental impact (Fig. 8.4). In fact, as above reported, it was estimated that an integrated membrane-based system with membrane crystallizer units working on NF and RO retentate streams, like the one schematized in Fig. 8.4, could increase plant recovery until 92.4% [25]. From an energetic point of view, the introduction of MCr introduces, with respect to an RO desalination process, a thermal energy requirement. Total energy consumption for a system like the one reported in Fig. 8.4 can be as high as 26.91 KWh/m^3. However, the possibility to work at relatively low temperatures (30–90 °C) provides the chance to utilize waste heat or other sustainable energy resources (such as geothermal or solar energy) thus lowering energy consumption until 1.61 KWh/m^3 [25].

Other examples can be found in the Megaton project in Japan [28] and in the SEAHERO project in South Korea [29]. In the first part of the projects the emphasis has been mainly on increasing the desalination capacity. However, in the second part of the projects the brine disposal issues is also addressed. Hybrid systems with MD and PRO units are proposed for the extraction of valuable resources from the brine, the minimization of the environmental impact of the brine, and the recovery of energy. Moreover, SEAHERO project has suggested a hybrid system forward osmosis/reverse osmosis for increasing the recovery factor by 30% and hereby reducing the brine volume in the same extend. This hybrid desalination process can minimize the energy consumption to less than 2.5 kWh/m^3 and water price to 0.6 $/ton. Another interesting example of the fast growing interest toward minerals/water/energy production from the sea can be found in the 5 years Global MVP research program (2013–2018) in progress in Korea [30]. This is a R&D program attempting to go beyond RO technologies and in which MD, valuable resource recovery, and PRO are the main objectives and goals.

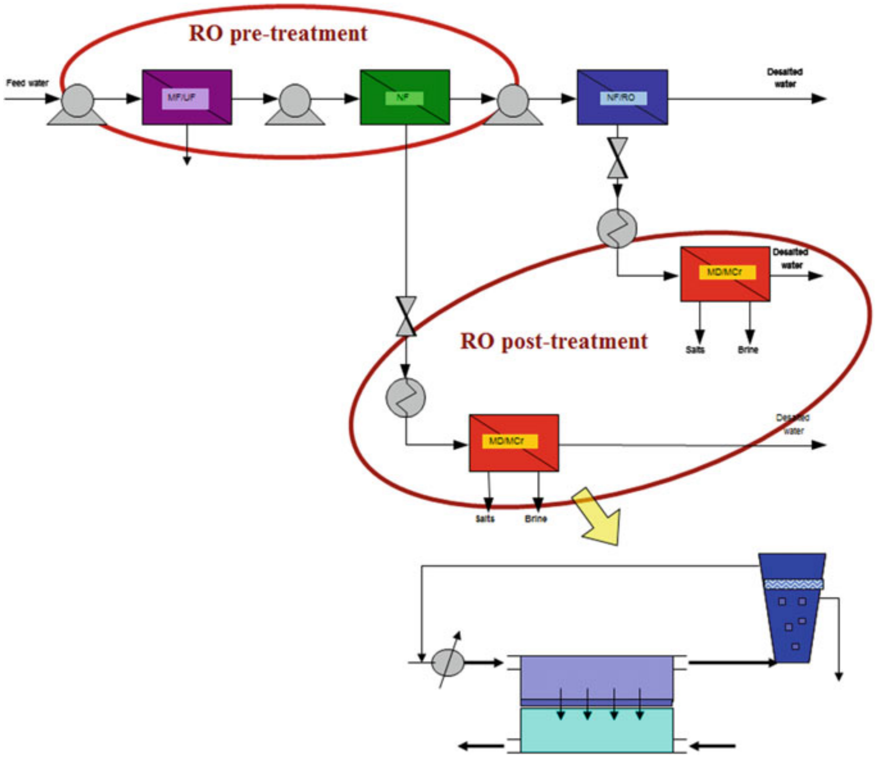

Fig. 8.4 MEDINA strategy (as described in [25])

8.4 Membrane Technology for Energy Production

Membrane engineering is contributing in a positive way not only to minimize water shortage and raw materials depletion, but also to provide the possibility to produce energy from clean and sustainable sources. A sustainable energy resource, independent from solar radiation or wind power, is the salinity gradient energy, also called *blue energy*. The latter is the energy that can be obtained mixing water streams with different salt concentrations. Blue energy is available where freshwater streams flow into the sea or it can be made available from natural or industrial salt brines.

In general, all techniques currently available for salty water treatment could be used to generate power from salinity gradients when operated in the reversed mode, such as pressure-retarded osmosis (PRO—Fig. 8.5 and reverse electrodialysis (RED—Fig. 8.6).

In PRO, two solutions of different salinities (for example, freshwater and seawater) are brought into contact by a semi-permeable membrane. It is well known that chemical potential difference between the solutions causes the transport of the

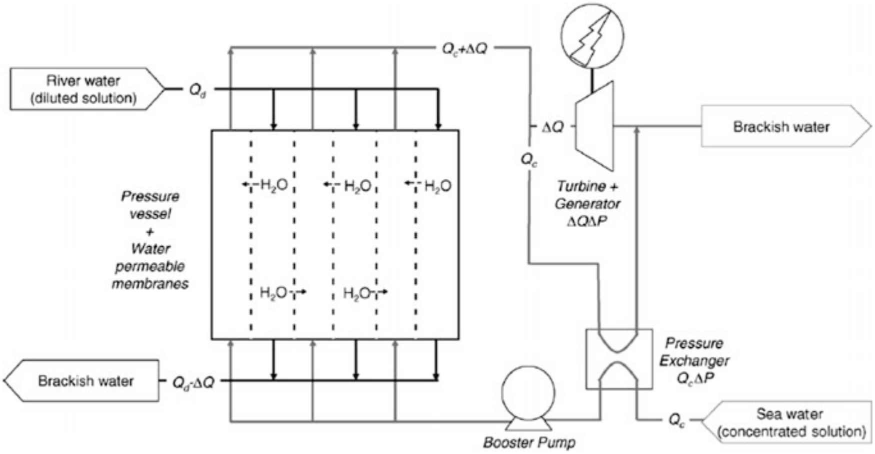

Fig. 8.5 Conceptual representation of an energy conversion scheme using pressure-retarded osmosis. Reprinted with the permission from Ref. [31]. Copyright 2007 Elsevier

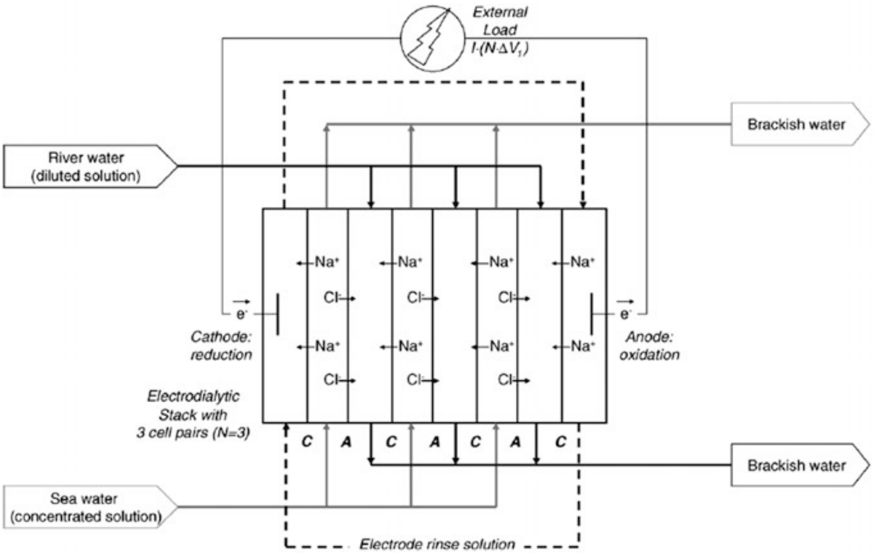

Fig. 8.6 Conceptual representation of an energy conversion scheme using reverse electrodialysis. Reprinted with the permission from Ref. [31]. Copyright 2007 Elsevier

solvent (i.e., water) from the diluted salt solution to the more concentrated salt solution. If hydrostatic pressure is applied to the concentrated solution, the transport of water will be partly retarded. The transport of water from the low-pressure diluted solution to the high-pressure concentrated solution results in a pressurization of the volume of transported water [31]. This pressurized volume of transported water can be used to generate electrical power in a turbine.

RED is based upon the transport of the ions through a stack of cationic and anionic membranes. The compartments between the membranes are alternately filled with a concentrated and a diluted salt solution. The salinity gradient results in a potential difference over each membrane. This chemical potential difference causes the transport of ions through the membranes from the concentrated solution to the diluted solution. The potential difference over the electrodes can be used to generate electrical power, when an external load or energy consumer is connected to the circuit [31].

PRO and RED have their own field of application: PRO seems to be more adaptable to generate power from concentrated saline brines because of the higher power density combined with higher energy recovery. For the same reason, RED seems to be more attractive for power generation using seawater and river water [31].

W. Post et al. [31] estimated that the global energy output from estuaries is 2.6×10^{12} W, which is approximately 20% of the present worldwide energy demand. Skilhagen [32] estimated that the cost of energy from osmotic power is 50–100 €/MWh, which is comparable and competitive with other new renewable energy sources such as wave and wind.

Although the salinity gradient power was recognized more than 50 years ago, many research and development issues, especially those related to membrane properties and costs, still need to be resolved before PRO and RED are available for large-scale commercial application. However, a reconsideration of these membrane processes is worthwhile due to the declining membrane costs, to the increasing prices of fossil fuels and to the possibility to redesign desalination plants for water and energy production via the integration of RO (as desalination technology) and RED (as energy production technology).

A hybrid RED system using highly concentrated solutions recovered from a seawater desalination plant (based on RO or evaporation) and further concentrated by solar evaporation, and seawater (or brackish water) as the dilute solution has been proposed by Brauns [15]. Model simulations of this system indicate that the development of thin membranes with specific characteristics in terms of resistivity and permselectivity in an adequate RED stack design is necessary for producing a high RED output.

Different configurations of hybrid RED–RO processes have been studied and compared by Li et al. [33]. The performance of two basic modes (RED → RO and RO → RED) and two complex modes (RED → RO → RED and RED ↔ RO) was evaluated by determining their specific energy consumption and concentration level of the discharge brine. Their modeling results indicate that the RED–RO hybrid process configurations studied are superior to conventional SWRO processes in several aspects: (i) the total energy consumption can be markedly reduced with even an energy-gaining process being possible; (ii) the brine management is built into the hybrid process, which permits realizing a zero-discharge system with a higher recovery; and (iii) the RED–RO configuration can be easily modified to accommodate different requirements. Due to lack of experimental data, Li et al. [33] indicate that the studied and proposed conceptual designs need systematic experimental verification in order to be validated.

A FP7 European funded project “Reverse Electrodialysis Alternative Power Production (acronym: REAPower), launched in 2010, had as objective to prove the concept of electricity production through Salinity Gradient Power-Reverse Electrodialysis (SGP-RE) using brine and sea or brackish water and to develop the necessary materials, components, and processes [34]. In order to overcome the main limitation of the combination of seawater and freshwater (i.e., the low conductivity of the compartments in the SGP-RE stack holding the freshwater), REAPower uses seawater as the low concentration solution and brine as the high concentration. The expectation is to deliver electricity at cost similar to wind power. Theoretical calculations, assuming similar conditions to the salt pond where the first RE stack for brine and seawater reverse electro-dialysis would be installed, showed that the theoretical osmotic energy content of 18,8 MJ/m^3 of brine could result in a power output of 450 kWe generating electricity at very attractive cost [35].

8.5 Economics of the Membrane-Based Desalination System with Md and/or Mcr Units

The cost of membrane desalination has decreased significantly over the past three decades, especially in the reverse osmosis process, while traditional water resources have become less available. Similarly, the cost of desalinated water continues to be higher than the cost of obtaining water from conventionally treated sources, such as surface water. Advances in technology may help both reducing the cost and enabling a more sustainable water supply. Reduction in seawater RO membrane desalination costs has been favored by the growth rate, plant capacity, competition with other technologies, and the fast improvements in RO systems (better process designs, membranes and materials, and lower energy consumption) as well as the simplicity and flexibility of recent project bids. As a result, N. Ghaffour et al. [36] report that the cost of desalinated seawater has fallen below US\$0.50/m^3 for a large-scale seawater reverse osmosis plant at a specific location and conditions while in other locations the cost is 50% higher (US\$1.00/m^3) for a similar facility (anyway and in both cases much lower than US\$2.10/m^3 as quoted in planning documents of 1975 [12]).

The total cost of desalinating water includes capital cost, annual operation, and maintenance costs. The capital cost is represented by the total construction and non-construction (engineering, commissioning, land acquisition, and legal and administrative fees) costs of the project and the interest on the capital over the loan payback period. The annual operation and maintenance costs are represented by the chemicals, power, equipment replacement, and labor costs. Several factors affect the capital, operating, and maintenance costs of desalination facilities. Some of them are included in Table 8.2. For the particular case of MD and MCr, both capital and operational costs mainly depend on system parameters such as flux as a function of flow rates and feed inlet temperature.

Many desalination plants built recently have greater desalinated water delivery costs caused by special circumstances, such as plant remediation or upgrades, local variation in energy costs, and site-specific issues in raw materials costs (e.g., tariffs and transportation) [33].

For what concerns integrated membrane-based desalination systems, costs of the desalination plant and of the produced water will have to be calculated considering with particular attention the raw materials and blue energy produced.

Economic evaluations of various membrane-based desalination processes with MD and/or MCr units can be found in Table 8.3. In these works different process designs were analyzed. Ohta et al. [34] and Drioli et al. [36] in 1990 and in 1999, respectively, estimated a desalted water cost equal to US\$1.25/m^3 for the integrated system *RO–MD* in which the RO brine was processed through MD in order to reduce the RO brine volume and to increase the total plant recovery factor. The utilization of NF as RO pretreatment and MCr as RO posttreatment (instead of MD) allowed Drioli et al. [37] to decrease the desalted water cost to US\$1.04/m^3 in 2002, with an overall water cost reduction of around 17%. Moreover, Drioli et al. [37] indicated that desalted water cost can be reduced until US\$0.52/m^3, in the same *NF + RO + (MCr on RO brine)* process, when thermal energy is available in the plant. The introduction of NF allows reducing cost because it has implications on the desalination process itself: turbidity, microorganisms, hardness, the most part of multivalent ions, and 10–50% of monovalent species (depending on NF membrane type) are retained through this operation. As a consequence, the osmotic pressure of the RO feed stream is decreased, thus allowing the unit to operate at higher recovery factors. Moreover, the integrated NF–RO process is more environmentally friendly, because less additives (antiscalants, acid) are needed.

Macedonio and Drioli [25], in 2011, evaluated water cost for the integrated membrane-based desalination system *MF + NF + RO + (MCr on RO brine)* in which MF was used as NF pretreatment. They estimated a desalted water cost equal to US\$0.441/m^3 when thermal energy is available in the plant. The adoption of MF

Table 8.2 Main factors affecting costs of desalination facilities

Capacity and location of the plant
Quality, salinity and variability of the available source water
Required water quality
Concentrate management plan
Co-location with existing power generation facilities
Plant life
Energy consumption and cost
Chemicals consumption and cost
Equipments replacement and frequency of replacement
Labor cost
Disposal cost

Table 8.3 Cost comparison of various membrane-based desalination processes[a] (From [25, 37–41])

Process	Cost per unit of permeate ($\$/m^3$)	Water recovery factor (%)	Year	Reference
RO–MD	1.25	87.6	1990, 1999	[38, 37]
NF + RO + (MCr on RO brine)	1.04	100	2002	[39]
NF + RO + (MCr on RO brine)–MCr with available heat energy	0.52	100	2002	[37]
MF + NF + RO + (MCr on NF brine)	0.675	71.5	2011	[25]
MF + NF + RO + (MCr on NF brine) and electrical energy recovery device	0.639	71.5	2011	[25]
MF + NF + RO + (MCr on NF brine) and electrical energy recovery device—MCr with available heat energy	0.513	71.5	2011	[25]
MF + NF + RO + (MCr on RO brine)	0.596	69.9	2011	[25]
MF + NF + RO + (MCr on RO brine) and electrical energy recovery device	0.560	69.9	2011	[25]
MF + NF + RO + (MCr on RO brine) and electrical energy recovery device—MCr with available heat energy	0.441	69.9	2011	[25]
MF + NF + RO + (MCr on NF and RO brine)	0.730	92.4	2011	[25]
MF + NF + RO + (MCr on NF and RO brine) and electrical energy recovery device	0.703	92.4	2011	[25]
MF + NF + RO + (MCr on NF and RO brine) and electrical energy recovery device—MCr with available heat energy	0.515	92.4	2011	[25]
MF + NF + RO + (MCr on NF) + (MD on RO brine)	0.739	88.4	2011	[25]
MF + NF + RO + (MCr on NF) + (MD on RO brine) and electrical energy recovery device	0.710	88.4	2011	[25]
MF + NF + RO + (MCr on NF) + (MD on RO brine) and electrical energy recovery device—MD/MCr with available heat energy	0.514	88.8	2011	[25]
MF + MD[b]	from 1.28 to 0.72	66.3	2014	[40]
Pretreatment + MCr[b]	from 4.81 to 2.61	34.1	2015	[41]

[a] Potable water cost calculated not considering the gain for the salts sale

[b] Feed is produced water and not seawater

as NF/RO pretreatment allows reducing water cost because it provides an NF/RO feedwater of good quality. The total costs for the MF are lower than that of a conventional pretreatment because of (i) less membrane replacement cost due to the lengthened membrane useful life; and (ii) less chemical consumption and cost because less chemicals are needed for disinfection, coagulation, and dechlorination.

An integrated *pretreatment (based on MF + activated carbon filtration*) *+MCr* system was utilized for water and salts production also from produced water by Ali et al. [41]. Produced water represents the largest wastewater stream from oil and gas production. Generally, its high-salinity level restricts the treatment options and poses serious environmental threats. Ali et al. [41] estimated a desalted water cost ranging from US\$4.81/m^3 to US\$2.61/m^3, depending on the membrane module utilized and on the feed inlet temperature. The highest water cost of *"pretreatment* + *MCr"* system with respect to an *"MF* + *NF* + *RO* + *(MCr on RO brine)"* system is due to the fact that in the first process the whole feed is desalted through MCr unit. The latter MCr needs thermal energy and works at lower flux with respect to RO, thus requiring higher membrane and energy cost for achieving the same water recovery. On the other side, MD and/or MCr showed an excellent rejection both of the total solids and carbon present in the feed water and, therefore, could represent a proper treatment of produced water thus solving the environmental concerns of its disposal. On the other side, Macedonio et al. [40] report that produced water treatment through an integrated *MF* + *MD* system could be a cost-competitive technology because the obtained water cost (US\$1.28/m^3 ÷ US \$0.72/m^3) is intermediate between those found in literature for thermal processes operated at higher temperatures (US\$ 1.00/m^3 for multiple effect distillation, US \$1.40/m^3 for multistage flash) [40].

No water cost reported in Table 8.3 considers the gain for the salts sale. The latter represents a benefit of the desalination plant, an additional gain to that of water. With this strategy, the costs of desalination plant and of the water produced have to be calculated considering the salts produced and, in particular, the high quality of the produced crystals [22, 23, 27, 28, 39]. Various examples can be found in Table 8.4. It can be observed that considering the high quality of the NaCl salts obtained via MCr from produced water, Ali et al. [41] report that the water cost drops to 1.24 ÷ 3.44 \$/m^3 (depending on the membrane module utilized) when the salts sale is taken into account in the economical evaluation. For what concerns the desalination of seawater, the integrated systems with MCr unit produce an amount of salts so high to strongly reduce the cost of the desalination process, as it can be seen for the system with MCr operating on NF brine where water desalted cost is reduced until 0.256 \$/m^3 (Table 8.4), i.e., a 62.07% reduction. Moreover, in the system with MCr operation on both NF and RO retentate streams, the gain for their sale covers more than entirely the cost of the desalination process (Table 8.4). Therefore, these processes become attractive also from an economical point of view, not to mention the environmental benefits due to the minimization of waste disposal.

Table 8.4 Cost comparison of various membrane-based desalination processes with MCr unit in which the gain for the salt sale is taken into account

Process	Amount of recovered salts (Kg/h)	Cost per unit of permeate ($\$/m^3$)	Year	Reference
Pretreatment + MCr[a, b]	n.a.	from 3.44 to 1.24	2015	[39]
MF + NF + RO + (MCr on NF brine)[c]	5648	0.256	2011	[25]
MF + NF + RO + (MCr on RO brine)[d]	14875	−0.017	2011	[25]
MF + NF + RO + (MCr on NF) + (MCr on RO brine)[c]	20523	−0.058	2011	[25]
MF + NF + RO + (MCr on NF) + (MD on RO brine)[c]	5648	0.400	2011	[25]

[a] Feed is produced water and not seawater

[b] Recovered salts: NaCl

[c] Recovered salts: $CaCO_3$, NaCl, $MgSO_4*7H_2O$

[d] Recovered salts: $CaCO_3$, NaCl

8.6 Concluding Remarks

In the last decades, membrane operations have been already assigned a key role in water reclamation schemes that are aimed at higher water quality reuse applications. An example can be found in desalination industry. Ghaffour et al. [36] report that the total global desalination capacity was around 66.4 million m^3/day in 2013 and it was expected to reach about 100 million m^3/day by 2015. Of the global desalted water, 60% of the total capacity is produced by reverse osmosis technology [12]. The success of RO treatment was due to the improvements in membrane performance (better membranes and materials, increased salt rejection and flux, improved membrane life and process designs), to the lower energy consumption, to the improvements in pretreatment processes, and to the increase in plant capacity.

Despite the enormous success of membrane desalination technology, improvements are still required in terms of desalted water cost, higher productivity (that means higher water recovery factors), better water quality, and enhanced eco-sustainability of the desalination process (solving brine disposal problem). At present, the battle against membrane fouling and in particular against biofouling seems to be the most critical issue to face. Fouling is caused by the deposition of materials on or within the structure of the membrane, which results in increase in hydraulic resistances, operational and maintenance costs, and deterioration of productivity and product quality. Biological fouling is caused by the development of colonies of bacteria or algae on the surface of the membrane. Fouling and biofouling affect membrane lifetime, with important relapse on membrane replacement rates that usually range between 5 and 20%, depending on the nature of feed water (the lower limit applies to low-salinity brackish water, the upper limit is valid for high-salinity seawater) and on the utilized pretreatment procedures. Research efforts are therefore addressed to a better understanding of the biofouling characteristics in order to delay the time of biofilm formation, to implement effective biocontrol protocols, and to identify proper operating procedures for cleaning the biofouled membranes. An efficient pretreatment is also crucial for an adequate control of fouling phenomenon. As discussed in the chapter, MF/UF technologies are today more and more considered as pretreatment for RO plants with superior quality performance than conventional technology, and the higher investment cost (in comparison with conventional in-line flocculation and media filtration) is almost completely compensated by costs reduction in the successive RO stage, by enabling higher permeate flux, recovery factor, and longer membrane lifetime.

Brine disposal is another crucial problem of seawater desalination processes. Recently, the increasing number and capacity of installed desalination plants exacerbated the problem of the negative environmental impacts of producing concentrate wastes. Cost-effective and environmentally sensitive concentrate management is today recognized as a significant hurdle to extensive implementation of desalination technologies. At present, the most part of desalination facilities discharge their concentrate waste stream into surface waters or the ocean. Membrane engineering can help minimize this problem by a proper redesign of desalination processes, by combining various membrane operations. As a matter of fact, reverse osmosis can be utilized completed with other membrane operations. Traditional membrane separation systems, such as micro-, ultra-, and nano-filtration, can be utilized as RO pretreatment whereas MD/crystallization as RO posttreatment. MD/MCr technology offers a powerful tool for inter-phase mass transfer driven by partial pressure gradients, not limited by concentration polarization. In principle, water recovery factors up to 90% can be reached; in addition, the ability to concentrate RO or NF brines above supersaturation limit might offer the opportunity to recovery salts dissolved in seawater (sodium chloride, epsomite, etc.) as crystalline product. Moreover, also blue energy production from salinity gradients through PRO or RED might be integrated in the system. In this logic, desalination can be considered a process for desalted water recovery, minerals extraction, and energy production from seawater thus approaching the concept of “zero-liquid-discharge” and “total raw material utilization”.

However, a better understanding of material properties and transport mechanisms as well as the development of innovative nanostructured membrane materials with improved properties (including selectivity and flux), appropriate module and process design, and, in general, a deeper engineering analysis, is fundamental for boosting efficiency in membrane technology applications.

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Chapter 9
Removal of Toxic Compounds from Water by Membrane Distillation (Case Study on Arsenic)

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Abstract Contamination of groundwater by arsenic (As) is a global health hazard affecting more than 150 million people over 100 countries around the world. There are several treatment options available for removal of arsenic from water, both on-site and off-site, and the most commonly used technologies are oxidation with filtration, biological oxidation, co-precipitation followed by adsorption onto coagulated flocks, ion exchange, adsorption onto various solid media and membrane technology. These technologies are well established for arsenic removal from aqueous solutions; yet all of them have drawbacks and their by-products can be a further potential source for secondary arsenic pollution. Membrane Distillation is promising technology that can be utilized in arsenic removal from contaminated water to meet the maximum contaminant level of 10 µg/L as set by WHO. However, only very few lab-scale investigations demonstrated the technology's potential. Lab-scale tests and MD prototypes have been utilized in several arsenic removal tests and studies with different MD configurations and membranes materials. In addition, studies have been conducted on integrated systems with other treatment technologies and integrated systems producing several water and energy services. Test results showed that MD had achieved high removal percentages of more than 99% with stable production rates.

Keywords Arsenic · Removal technologies · Membrane technologies · Membrane distillation

Abbreviations

WHO	World Health Organization
MCL	Maximum concentration limit

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NF	Nanofiltration
MF	Microfiltration
RO	Reverse osmosis
UF	Ultrafiltration
MD	Membrane distillation
TDS	Total dissolved solids
PTFE	Polytetrafluoroethylene
PP	Polypropylene
PE	Polyethylene
PVDF	Polyvinylidene difluoride
AGMD	Air gap membrane distillation
DCMD	Direct contact membrane distillation
FVMD	Flash vaporization membrane distillation
PET	Polyethylene terephthalate
VMD	Vacuum membrane distillation
FO	Forward osmosis
COD	Chemical oxygen demand
HOVs	Halogenated volatile organic compounds
VOCs	Volatile organic compounds
LPP	Liquid-phase precipitation
TRU	Transuranic waste
PhACs	Pharmaceutically active compounds
SEM	Scanning electron microscope
EDS	Energy dispersive spectroscopy

9.1 Introduction

Contamination of groundwater by arsenic (As) is a global health hazard affecting more than 150 million people over 100 countries around the world from USA to Thailand, China, India, Bangladesh, and other countries [1–3]. Most of the affected parts of the world belong to the developing countries in Southeast Asia where the problem constitutes a major health issue particularly during the dry seasons. Arsenic contamination and its mitigation is a priority area in drinking water quality within the World Health Organization (WHO), national and international agencies [4, 5]. According to WHO, the maximum allowable concentration of arsenic (MCL) in drinking water is 10 μg/L [6, 7]. Elevated concentrations of arsenic in groundwater well above the MCL have been reported in various parts of the world with concentrations reaching up to 2000 μg/L [8]. The variant socio- economic and political contexts, in addition to the unavailability of affordable different treatment technologies resulted in somewhat higher MCL standards in different countries.

9.1.1 Arsenic Occurrence in Nature

The primary source of arsenic in the environment is the release of arsenic-bearing minerals [9]. Arsenic may occur naturally in some 200 minerals in varying degrees as elemental arsenic, arsenides, sulfides, oxides, arsenites, and arsenates [7, 10]. Anthropogenic activities also contribute to the release of arsenic through the use of insecticides, herbicides, and phosphate fertilizers, semiconductor industries, mining, industrial processes, coal combustion, etc. [9]. In nature, arsenic exists in both organic and inorganic forms. The organic species are abundant in seafood and less harmful to the human health, readily eliminated by the body, while the inorganic forms are more dominant in water and more toxic [3].

In groundwater, arsenic exists primarily as oxyanion in two oxidation states: arsenic As III (arsenite) and arsenic As V (arsenate). Both As III and As V are thermodynamically stable form of inorganic arsenic in water and exist within the pH range of 6–9 [6, 11]. While As (V) is predominant in oxic groundwater in the major forms of H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}; As (III) is more dominant in anoxic environments with H_3AsO_3 and $H_2AsO_3^-$ being the common forms [1, 7].

9.1.2 Arsenic Effect on Health

As stated earlier, arsenic contamination is considered to be a serious health issue in several parts of the world. It is a well-established fact that arsenite (As III) is more toxic than arsenate (As V), with inorganic arsenic being more toxic than organic arsenic [1, 10, 12, 13]. Humans are exposed to arsenic in different ways: directly through drinking water or indirectly in terms of food consumption [9]. Exposures to arsenic is reported to cause various types of diseases, including non-pitting edema, skin thickening, neurological disorders, muscular weakness, respiratory diseases, gastro-intestinal, liver and cardiovascular problems, and several cancer types including urinary bladder, lungs, skin, kidneys, nasal passages, liver, and prostrate. [2, 9, 12, 14].

9.2 Arsenic Removal Technologies

There are several treatment options available for removal of arsenic from water, both on-site and off-site. The most commonly used technologies are oxidation with filtration, biological oxidation, co-precipitation followed by adsorption onto coagulated flocks, ion exchange, adsorption onto various solid media, and membrane technology [3, 7, 15]. All of the these methods are well established for arsenic removal from aqueous solutions; yet all of them have drawbacks and their by-products can be a further potential source for secondary (As) pollution [7]. Among others, the successful removal of arsenic depends highly on the chemistry and composition of the contaminated water, and in particular, the arsenic form. As most of arsenic exist in the arsenite form (As III), oxidation of As III to As V is necessary to achieve the satisfactory results of arsenic removal [9]. Compared with membrane technology, physicochemical processes have some drawbacks in terms of the requirements of multiple chemical treatments, pre- or post-treatment of drinking water, high running and capital cost and more importantly, regeneration of medium (in case of use of ion exchange resins or adsorbent materials) and handling of arsenic-contaminated sludge (if coagulation is employed) and the disposal of the sludge, which poses a problem in most cases [4, 7, 10, 16]. In membrane technologies, the change in arsenic rejection, depending on the water pH and the kind of membrane used (for NF and RO), is a drawback of such technologies. All the treatment technologies remove (As V) much better than (As III) [17], requiring, therefore, a pre-oxidation stage, which in turn will require use of chemicals, increased cost, and a decrease of plant safety due to the use of typical oxidizing agents like ozone, hydrogen peroxide, and chlorine [16].

The choice of a suitable treatment option for water supply depends on a number of factors, including the maximum allowed arsenic concentration, water quality characteristics, the status of the existing treatment system and their ability to be modified, and other water quality parameters that must be met along with the arsenic standard in addition to residual/waste management and cost [15].

Removal efficiency of different processes is less than 95% for physicochemical processes and more than 95% for membrane technologies, except for membrane distillation (MD) where it is greater than 99% [5]. Most of the membrane-based arsenic removal studies are concentrated on reverse osmosis (RO) and nanofiltration (NF) as they are the most dominant and efficient membrane technologies, and successfully applied in water treatment/desalination plants around the world. It is generally reported that NF can achieve removal efficiencies of As (III) from 20 to 85% and from 50 to 85% for RO depending on the types of membranes and the pH of the solution. The removal efficiency of As (V) by RO and NF has been reported to vary from 80 to 97%, depending on the membrane properties and pH of the solution [2].

9.2.1 Oxidation

The purpose of oxidation is to convert soluble As (III) to As (V), which is followed by precipitation. As arsenite (As III) is the dominant form of arsenic in anaerobic groundwater, the process is an essential pretreatment step. The oxidation of As (III) into As (V) is achieved by chemical oxidants such as chlorine (Cl_2), chlorine dioxide (ClO_2), ozone (O_3), hydrogen peroxide (H_2O_2), chloramine (NH_2Cl), permanganate (MnO_4^-), and ferrate (FeO_4^{2-}) [1, 9]. Oxidation is considered a simple and cheap method; however, it is slow and produces toxic by-products. Oxidation alone is not considered as an effective method for removal of arsenic [14] and must be followed by the second step.

9.2.2 Adsorption Processes

The most common method of arsenic removal from water and wastewater is the use of different adsorbents [13]. Adsorption is a process that uses solids for removing substances from either gaseous or liquid solutions. Generally, the removal of arsenic by adsorption techniques depends on pH and the speciation of As. At pH lower than 7, As (V) removal is better compared to the As (III) [7]. The capacity and adsorption rate depends on the presence of other ions like PO_4^{-3}, SiO_4^{-4}, HCO_3^-, and Ca^{2+} competing for the adsorption sites [9]. Removal of arsenic by adsorption onto activated/coated surfaces is getting popular because of its simplicity and applicability, especially in rural area, with several of the adsorbents regenerated and reused [1, 3]. Adsorbents are broadly divided into two classes: (1) commercial and synthetic activated carbons and (2) low-cost adsorbents such as agricultural and industrial by-products, clay, oxides, and bio-sorbent. Iron or iron compounds (iron oxides, oxy-hydroxides and hydroxides) are the most widely used adsorbents, due to their higher removal efficiency at lower cost compared with other adsorbents [9, 11, 14].

Adsorption is a relatively cheap process and can achieve high removal efficiencies, in addition to being applicable for a wide range of pH solutions. Regeneration problems [14] and arsenic-rich sludge, which need to be carefully disposed, are the major disadvantages of the process [3, 7].

9.2.3 Coagulation–Flocculation

The process is achieved by the addition of a coagulant followed by the formation of a floc, which is a method that has been used to remove arsenic from groundwater. Positively charged cationic coagulants reduce the negative charge of the colloids, resulting in formation of larger particles due to mass build-up of particles called flocs which are precipitated by gravity or filtrated by membranes [7, 9]. Soluble arsenic is precipitated/co-precipitated onto the flocs and is thus eliminated from aqueous solution. The most common coagulants for arsenic removal are the Fe and Al based coagulants [1, 7]. The commonly used chemicals are aluminum salts such as aluminum sulfate [$Al_2(SO_4)^{3-}\cdot 18H_2O$] and ferric salts such as ferric chloride [$FeCl_3$] or ferric sulfate [$Fe_2(SO_4)^{3-}\cdot 7H_2O$] because of their low cost and relative simple handling [9].

Coagulation is considered simple and cost-effective. However, the process generally requires a centralized treatment facility and cannot be economically employed in rural water supply systems [15]. Other major limitation of the process is the production of a large amount of arsenic-rich sludge that needs to be safely handled. The disposal of this sludge can affect the cost of this process, especially if the sludge is classified as hazardous waste [17], in which case, the waste management of such sludge reduces the feasibility of applying this method in field conditions [3, 7].

9.2.4 Ion Exchange

Ion exchange is a physical/chemical process by which an ion on the solid resin is exchanged for an ion in the feed water. Anion exchange resins are commonly used for the treatment of arsenic where the oxy-anionic species of arsenate ($H_2AsO_4^{1-}$, $HAsO_4^{2-}$ and AsO_4^{3-}) are exchanged with the anionic charged functional group of the resin [9, 18]. Oxidation of As (III) to As (V) is an important pretreatment step for ion exchange processes [7, 9]. The process is pH independent and generally effective; however, ion exchange method is only applicable for low TDS. In addition, the method has other disadvantages including physical pretreatment, post-treatment, high running and capital cost and production, and handling of arsenic-contaminated sludge [10].

9.2.5 Membrane Processes

Membrane processes are becoming more popular in water treatment plants and considered a promising technology for removing arsenic from groundwater. There are four major membrane processes; microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The separation by these processes depends on the pore size of the membrane [18, 19] and for MF and UF, separation is achieved via mechanical sieving while for NF and RO, separation is achieved by capillary flow or solution diffusion [7, 18]. The negatively charged membranes allow a higher rejection obtained with anionic components, like As (V), which require the oxidation of As (III) into As (V). Advantages of membrane technologies include the effective removals, no solid waste generation and the ability to remove other toxic and impurities in the same process. Disadvantages of membrane processes include the use of oxidizing agents (oxidation from As (III) to As (V) is still needed) and high capital and operation cost [3].

The MF is a low-pressure-driven membrane process used for separating colloidal and suspended particles in the range 0.1–10 μm [9]. MF membranes are only able to remove particulate form of arsenic from water, since the size of the soluble arsenic is small enough to pass through the pores of the MF membrane [19]. Thus, increasing particle size of arsenic-bearing species through a pretreatment step prior to MF is crucial. Coagulation and flocculation process is a typical pretreatment step [9, 19].

Ultrafiltration (UF) is also a low-pressure-driven membrane separation process having pore sizes in the range from 0.01 to 0.1 μm [9]. Similar to MF, the pores of the membrane are larger than the dissolved arsenic in contaminated water. Thus UF process needs to be combined with other processes such as coagulation and flocculation and adsorption [7]. For example, As (III) and As (V) bind or adsorb onto the surface of the cationic surfactant (such as cetylpyridinium chloride) forming aggregate molecules (micelles) which are large enough to be removed by UF [7, 9]. In addition, electro-charged UF has been used to enhance the arsenic rejection [18, 19] by increasing the repulsion between the negatively charged UF surface and anionic arsenic species.

NF and RO are high-pressure techniques and are able to remove dissolved arsenic from water, with both As (V) and As (III) effectively removed (up to 99%) [7]. NF membranes are generally negatively charged and the separation of arsenic is achieved by electrostatic repulsion between the anionic arsenic species and the charge of membrane as well as the small size of the pores of the membrane [7]. NF operates at lower pressures than reverse osmosis with several research bench-scale data indicating that high arsenic removals of 90% could be obtained using such method [17]. However, the removal efficiency of As (III) is much lower, about 20–30% [6], which results in general low rejection ratio in As (III) dominant water. In such condition, a pretreatment step is also crucial for achieving high removal rates. It was reported that a hybrid treatment system consisted of an oxidation unit integrated with a cross-flow nanofiltration membrane module can achieve about 96–98% arsenic removal efficiency [20].

Reverse osmosis (RO) uses a semipermeable membrane through which water permeates via a solution–diffusion mechanism [11]. In RO, pressure greater than the natural osmotic pressure is applied to the feed side of the membrane to drive the process. The RO membrane has pore size smaller than 0.001 μm and very high rejection rates can be achieved. As (V) removal efficiencies above 90% have been achieved with the RO system operated at high pressure, while As (III) removal efficiency was less than 70% [9]. The As (III) rejection in solution below pH 10 is low due to the existence of uncharged As (III) species, and in the case of As (III) dominant groundwater, the arsenic removal efficiency decreased to less than 50%, requiring oxidation as a pretreatment step in order to achieve high rejection ratio [6, 7, 9]. Additional drawback of RO is the high energy consumption and the high capital and maintenance cost. Table 9.1 summarizes the main characteristics of the aforementioned technologies.

9.3 Membrane Distillation

9.3.1 Introduction

Membrane distillation is a thermal water purification technology that utilizes a microporous membrane to create a liquid–vapor interface between two solutions with different temperatures. Only vapor can pass through the membrane pores from

Table 9.1 Summary of the main characteristics of arsenic removal technologies [1, 3, 4, 6, 7, 9–11, 14–17]

Technology	Main advantages	Main disadvantages	Energy/material needed	Cost level
Oxidation	• Simple • Cheap	• Slow • Produces toxic by-products • Step is not enough	Cl_2, ClO_2, O_3, H_2O_2,NH_2Cl, MnO_4^-,FeO_4^{2-}	Low
Adsorption	• Relatively cheap • High removal efficiencies	• Regeneration • Produces arsenic-rich sludge	Activated alumina, activated carbon, iron compounds	Low
Coagulation-flocculation	• Simple and cost-effective • Applicable for a wide range of pH solutions.	• Require a centralized treatment facility • Economically infeasible in rural area • Production of a large amount of arsenic-rich sludge • High demand for chemicals	Fe and Al salts ($Al_2(SO_4)_3$, $FeCl_3$	Low to medium
Ion exchange	• pH independent • Generally effective	• Only low TDS • Pretreatment • Posttreatment • Production of arsenic-contaminated sludge	Anion exchange resins	High
MF/UF	• Effective removals • No solid waste generation	• Combination with other pretreatment maybe needed • Oxidation is needed	High energy demand	Medium to high
NF/RO	• High separation efficiency • Ability to remove other toxic in the same process	• Pretreatment • Oxidation is needed	High energy demand Oxidizing agents	High

the high-temperature solution and it condenses on the lower temperature liquid solution/condensation surface. Membranes with pore sizes ranging from 0.01 to 1 μm are generally used. Hydrophobic, microporous membranes made of polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE), polyvinylidene difluoride (PVDF) are used in MD process [4]. The main requirement for MD process is that the membrane should not be wetted.

9.3.2 *Experimental Investigations on Removal of Arsenic by Membrane Distillation*

Though MD can be a potential option for arsenic removal from contaminated water to meet the maximum contaminant level of 10 μg/L as set by WHO, only very few lab-scale investigations demonstrated its potential [5]. The following paragraphs list these investigations in short.

Khan and Martin [21] used AGMD household water purifier prototype with 2 L/hour capacity made by HVR Water Purification AB, Stockholm to investigate MD in producing arsenic-free drinking water. The AGMD module used by the researchers consisted of 42 cm × 24 cm × 2.4 cm cassette containing two PTFE membrane sheets of a total area of 0.19 m^2 with a porosity of 80% and thickness of 0.2 mm. The AGMD experiments consisted of analyzing the performance of the system under different operating conditions. Feed cooling temperatures ranged from 15 to 70 °C, and hot side temperature was kept constant at about 80 °C. Arsenic-spiked tap water along with arsenic-contaminated groundwater was used with electrical conductivity of 250 μS/cm. The arsenic-spiked water sample was synthesized from $CaSO_4 \cdot 2H_2O$, $MgSO_4$, Na_2CO_3, and KNO_3. Arsenic concentrations were 266, 1800, and 300 μg/L for the three contaminated groundwater samples, while As-spiked samples concentrations were 1800–300 μg/L. The product water conductivity was around 0.6–1.5 μS/cm. The product water analyses of the three different feeds showed arsenic concentration below 0.4 μg/L for contaminated groundwater and below 0.03 μS/cm for As-spiked samples. The study showed that the results were not affected by operating parameters within the test range [21].

These results obtained by Khan and Martin [21] were employed in a study by Khan et al. [22] to assess an integrated biogas based poly-generation system to provide safe drinking water together with other necessary services needed in rural areas in Bangladesh, namely electricity and biogas. Figure 9.1 illustrates the integrated poly-generation system.

The study included a techno-economic performance for the system for meeting the demand of 30 households in a rural village. The analysis indicated that poly-generation system is much more competitive and promising in comparison

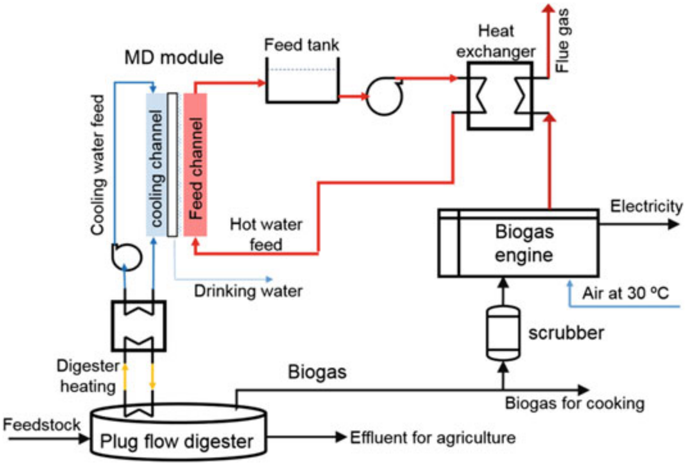


Fig. 9.1 Integrated systems for poly-generation of electricity, cooking gas and water production. Reprinted with the permission from Ref. [22]. Copyright 2014 Elsevier

with other available technologies when attempting to solve the energy and arsenic-related problems in Bangladesh. The payback period of such system was estimated to be between 2.6 and 4 years. However, the study pointed out some possible social, institutional, and financial barriers in the implementation and stressed the needs to be demonstrated via in-field trials [22].

The concept of poly-generation was revisited by the authors in another study featuring a PV array and animal and agriculture waste-fed digester, which in turn is coupled to a gas engine. The techno-economic analysis was performed for a poly-generation system to cover the demands of a village of 52 rural off-grid families. The leveled cost of the three major outputs was estimated: biogas for cooking (about 0.015 USD/kWh), hybrid generation of electricity (0.048 USD/kWh), and MD pure water (0.003 USD/liter). The payback period of such system was estimated to be between 3 and 4 years [23].

Manna and Pal [5] conducted experimental studies on removal of arsenic from contaminated groundwater using solar energy for phase change in a flash vaporization membrane distillation (FVMD) module. The module adopted the direct contact membrane distillation (DCMD) configuration and was fitted with PTFE membranes. The experimental setup (Fig. 9.2) consisted of a solar loop and FVMD loop, featuring evacuated tube collector coupled with a feed tank. The MD loop consisted of a flat sheet FVMD module in DCMD configuration that was designed to promote flash vaporization in the feed side of the module. A composite flat sheet PTFE membrane supported by a PP backing was used, with the membrane pore size of 0.22 μm and porosity of 80%. The groundwater of arsenic concentration 396 μg/L was used in the experiments and was used in the initial rejection experiments.

Additional synthetic arsenic was added to study the effect of increased arsenic concentration on the rejection efficiency with varying concentrations of 500–2000 μg/L. The synthetic arsenic-contaminated feed water contained As (V) arsenic compound sodium arsenate dibasic hydrate $Na_2HAsO_4.7H_2O$, and

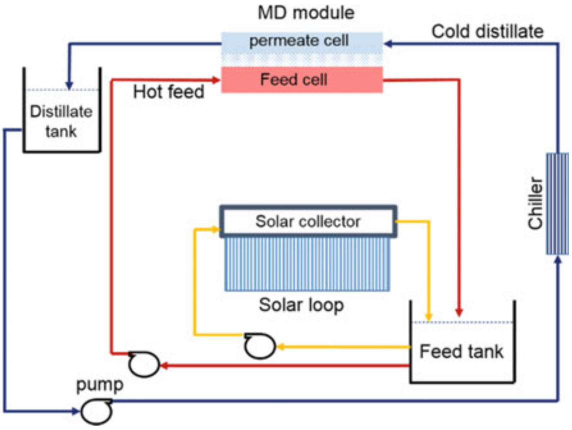


Fig. 9.2 Flow diagram of experimental setup for solar-driven FVMD process. Reprinted with the permission from Ref. [4]. Copyright 2010 Elsevier

trivalent sodium arsenite $NaAsO_2$. It was reported that the highest permeate flux was found to be around 53 L/m^2 h with more than 99% arsenic rejection [5].

Qu et al. [6] investigated As (III) and As (V) removal by direct contact membrane distillation (DCMD) with polyvinylidene fluoride (PVDF) membranes. 50 capillary membranes with an effective area of 12.56×10^{-4} m^2 were used. Arsenic solution was prepared using tap water with reagent-grade chemicals (As_2O_3 and $Na_2HAsO_3 \cdot 7H_2O$). Two sets of experiments were performed for separating As (V) and As (III) solutions; a concentration test to examine the maximum feed concentration at which the concentration in the permeate exceeds the 10 µg/L (MCL) threshold, and a long-term experiment to examine the integrity of the membrane and stability of the rejection. In the concentration test, As (V) in the permeate was not detected until As (V) feed concentration reached 1000 mg/L (starting from 0.2 mg/L). As (V) in the permeate continued to appear and exceeded the maximum contaminant limit when the feed As (V) reached 2000 mg/L, though the removal efficiency of As (V) concentration was above 99.99%. In the case of As (III) removal experiments, it was reported that the permeate As (III) was under the MCL until the feed As (III) increased to 40 mg/L, with a removal efficiency reaching 99.95%. In the long-term experiment which lasted for 250 h, the presence of As (III) and As (V) in the permeate was not detected during the whole process. In this last case, the initial feed concentration of arsenic was 0.5 mg/L and the permeate conductivity was stable at about 3.5 µS/cm, and the permeate flux was about 7.50 L/m^2 h. The difference in the removal efficiency of As (III) and As (V) in the concentration test was attributed to the different existing states between them. As (III) exists in a neutral molecular form, while As (V) exists in a negatively monovalent form. As the PVDF capillary membrane is negatively charged, As (III) is more difficult to be removed from water due to the lack of electrostatic exclusion. In all experiments, the mean feed temperature varied from 40 to 70 °C while the permeate temperature was kept at 20 °C [6].

Yarlagadda et al. [24] studied the feasibility of DCMD process to recover arsenic, uranium and fluoride from contaminated saline groundwaters (synthetic brackish water with 1000–10,000 mg/L) using two types of flat sheet membranes. PP membranes (nominal pore size of 0.22–0.45 µm, porosity of 70–75% and thickness of 110 µm) and PTFE membranes (nominal pore size of 0.22 µm, porosity of 80% and thickness of 60 µm). Synthetic water was prepared using reagent-grade chemicals and deionized water, and contained 10–400 µg/L of arsenic, prepared by adding ($Na_2HAsO_4 \cdot 7H_2O$) solution to the deionized water sample. Experiments were conducted for 12 h and for the highest arsenic, fluoride, and uranium feed concentrations, the resulting concentrations in the permeate were 0.17 µ/L, 0.56 mg/L, and 0.2 µ/L, for the three contaminants, respectively. The removal efficiency of these contaminants for most of the tests was in the range of 99–99.9%. It was reported that the DCMD process was tolerant of the chemicals present in the feed water and produced constant permeate rates irrespective of the contaminant concentrations, and that PTFE membrane produced a higher permeate flux rate compared with PP, though the contaminant removal rates were comparable between PP and PTFE membranes [24].

Solar energy was used to drive a DCMD unit to treat arsenic-contaminated water. Manna et al. [4] conducted experimental investigations on removal of arsenic from contaminated groundwater by employing a flat sheet PVDF membrane of 0.13 μm pore size, 0.0162 m^2 effective area, thickness of 150 μm, and porosity of 75%. The setup consisted of four components; a direct contact membrane distillation (MD) module, a solar energy collector (evacuated tubes), and two thermostatic baths. The feed temperature was varied between 40 and 61 °C. It was reported that the system produced almost 100% arsenic-free water from contaminated groundwater and fluxes as high as 74 L/m^2 h [4].

The same setup was used by Pal and Manna [2] to investigate arsenic removal from contaminated groundwater using three different types of hydrophobic membranes made of PTFE and PP flat sheet. Two of the three membranes were composite membranes having a thin PTFE active layer, while one has a PP support sublayer and the other a polyethylene terephthalate (PET) supporting sublayer. The third membrane was a symmetric and isotropic membrane made of pure polypropylene. Experiments were carried out using arsenic-contaminated groundwater collected from arsenic affected areas in India. Arsenic concentration ranged from 0 to 1200 μg/L with pH of 7.1–7.3. To study the effects of arsenic concentration on flux and distillate quality, the researchers simulated aqueous solutions prepared by dissolving quantities of analytical reagent-grade in ultrapure water. Arsenic trivalent sodium ($NaAsO_2$) was used to add As (III), while sodium arsenate dibasic hydrate ($Na_2HAsO_4{\cdot}7H_2O$) was used to add As (V) to the solution. In all the experiments the feed temperature was in the range of 30–61 °C. Fluxes as high as 74–95 L/m^2 h were reported and was attributed to a new concept in the design of lab-made flat module, where the membrane module was made of polycarbonate material with high thermal insulation property. The hydrodynamic design of the hot feed channel ensured that feed entered the module wide feed side channel through a very narrow circular conduit and underwent flash vaporization on exposure to the low pressure in the wide channel. This resulted in high rate of evaporation and promoted heat transfer through better mixing and minimizing temperature and concentration polarization. In conclusion, the researchers stated that almost 100% arsenic separation was achieved without wetting or damaging the membrane pores even after 120 h of operation [2, 4, 5].

VMD configuration was used by Criscuoli et al. [16] to treat water containing arsenic [As (III) and As (V)] at low feed temperatures (20–40 °C). Four flat microporous hydrophobic membranes were used in the experiments; two PP membranes and two PVDF with a membrane area of 0.018 m^2. Synthetic aqueous solutions of As (III) and As (V) were used and prepared using both distilled and tap water. As (III) were prepared by dilution of a mother solution of As (III) at 1000 mg/L, whereas solutions of As (V) were obtained by dissolving the desired amount of arsenic oxide trihydrate ($As_2O_5{\cdot}3H_2O$). The researchers came to similar conclusion of no presence of arsenic detected in permeate. Furthermore, they pointed out that there was no need for pre-oxidation step to convert As (III) into As (V), eliminating the use of chemicals consumption associated with such pretreatment step and hence, reduction of plant cost and complexity. However, fluxes obtained were relatively low due to the low temperature and flow rate operation conditions used in the experiments. Fluxes of 3 L/m^2 h were obtained, at feed temperature of 20 °C, while the highest flux of 12.5 L/m^2 h was achieved at 40 °C [16].

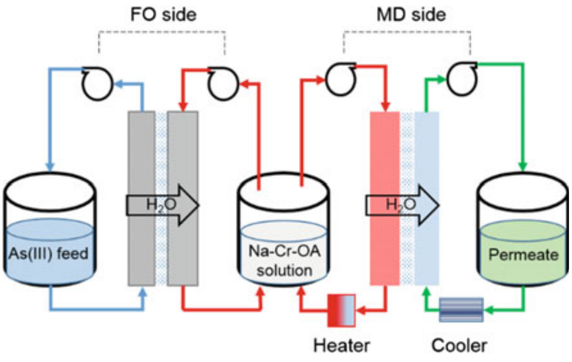
Adoption of VMD was also investigated by Dao et al. [3] for removal of arsenic from a shallow brackish groundwater in Vietnam. The study objective was to test arsenic rejection efficiency of the VMD process under presence of NaCl in feed solution. Synthetic brackish solutions containing NaCl (10 g/L) and As (III) with different concentrations ranging from 0.3 to 2 mg/L were used as feed solution in the study. All the tests were carried out with a bench-scale batch pilot plant utilizing a hydrophobic PTFE flat sheet membrane. The test results showed that VMD achieved high rejection rates for both As (III) and NaCl. As (III) concentrations in the permeate were always lower than the maximum contaminant level (MCL), regardless of feed As (III) concentration [3].

The integration of MD with other treatment technologies has been the subject of few researchers. Macedonio and Drioli [25] investigated possible integrated membrane system able to remove boron (WHO maximum concentration <0.3 mg/L) and arsenic from raw/brackish/seawater. Three different experiments were done; one considered RO alone, the second considered RO with oxidation as pretreatment [Since RO process is more effective in removing As (V) than As (III), the feed water was oxidized to convert As (III) to As (V)], and the third process is RO step followed by MD. As boron removal usually requires two RO stage treatment, in their suggested system, the researchers proposed that only part of the RO permeate (36.4%) can be further treated in the MD unit. In order to carry out the experimental tests, synthetic aqueous solutions have been prepared by dissolving the appropriate quantities of chemical reagents in demineralized water. The feed water arsenic concentration was equal to 0.4 mg/L. The membrane module used contained 40 polypropylene (PP) hollow fibers packed in a shell of 2.1 cm diameter and 60 cm length with a total membrane area of 0.1 m^2, pore size of 0.20 µm and in DCMD configuration. The concentrations of arsenic and boron in the permeate side of the three process were as follows; RO alone (14 µg/L; 0.45 mg/L), RO and oxidation (10 µg/L; 0.45 mg/L) and finally RO and MD (9 µg/L; 0.3 mg/L). The concentrations of arsenic and boron in the permeate of RO + MD setup are below the maximum allowable concentrations, according to which the researchers proves that MD can be used for total boron and arsenic removal from water without the need for the use of oxidant agents. The researchers concluded that the application of membrane distillation allows achieving removal efficiency value not easily reachable with other removal technologies [25].

Ge et al. [26] carried out a research on integrated system aiming at removal of As (III) from water by an oxalic acid complex with the formula of Na_3 [Cr $(C_2O_4)_3$] (Na–Cr–OA) via a forward osmosis–membrane distillation (FO-MD) hybrid system. Figure 9.3 shows a simplified process diagram.

MD module packed with 10 pieces of PVDF hollow fibers with 15 cm in length and effective area of 0.0043 m^2. The hybrid FO-MD experiments were conducted at 60 °C using a 1000 ppm As (III) feed solution and a 1.0 M Na–Cr–O draw solution

Fig. 9.3 Simplified process diagram of FO-MD hybrid system. Reprinted (adapted) with the permission from Ref. [26]. Copyright 2016 American Chemical Society



circulating in FO membrane module. The diluted Na–Cr–OA solution from the FO side and deionized permeate water at 20 °C were circulated in the MD membrane module. The hybrid FO-MD system was reported to be more efficient than the individual FO process in the concentration of the As (III) feed solution. The As (III) concentration in the MD permeate is lower than 0.01 ppm (10 µg/L) [26].

FO-MD integrated system was also used by Husnain et al. [27] for wastewater treatment and reuse. FO served as a pretreatment step to remove most contaminants in the feed water and MD was used to recover the draw solutes from FO effluent and produce high quality water. The feed solution contained 100–200 mg/L $NaAsO_2$, with initial As (III) concentration of 80–202 mg/L; As (V) concentration of 60–39 mg/L for two different samples was used. After 48 h of testing, a significant amount of As (III) was still observed in the draw solution indicating low rejection of As (III) by the FO membrane. The concentration of arsenic in the permeate of FO-MD for both As (III) and As (V) was below the detection limit of 0.2 mg/L (200 µg/L) corresponding to 99.9% removal. The researcher pointed out that the use high arsenic concentration in the feed and the use of instrumentation with relatively high detection limit was to demonstrate the high removal efficiency of the system. It is worth noting that the removal efficiency was also the same for other contaminants like ammonium and COD [27].

The integration of direct contact membrane distillation with acid-purged zero-valent-ion (DCMD-APZ) was studied by Abass et al. [28]. Three PTFE flat sheet membranes were for the removal of arsenic from As-spiked groundwater samples. The arsenic simulated solutions were prepared using analytical reagent-grade of $Na_2AsO_4 \cdot 7H_2O$ for As (V) and $NaAsO_2$ for As (III). The researchers reported that the DCMD-APZ configuration showed high arsenic removal up to 20 mg/L initial concentration with a maximum arsenic rejection efficiency greater than 90–99% removal with initial concentration of 100 µg/l. The distillate flux rate produced was in the range of 20–50 L/m^2 h. Furthermore, the technology was assessed as low maintenance technology with potential of producing higher distillate fluxes at lower cost compared with other stand-alone MD technologies [28].

The main results of aforementioned studies are summarized in Table 9.2.

Table 9.2 Summary of the main results from MD removal studies

Ref.	MD configuration	Study synopsis	Main results
[21]	AGMD/PTEF	Lab Equipment, 0.19 m^2, feed As concentrations 266–1800 µg/L	Product water As concentration from 0.6 to 1.5 µS/cm, not affected by operation conditions
[22]	AGMD	Modeling and feasibility study based on experimental work in ref. [21]; poly-generation of water electricity and biogas	Good potential; payback time 2.6–4 years; social and financial barriers in low-income communities
[23]	AGMD	Modeling and feasibility study based on experimental work in ref. [21]; integrated system of MD + PV array + biogas production for off-grid communities	Payback time estimated to be 3-4 years; biogas: 0.015 USD/kWh; electricity: 0.048 USD/kWh; pure water: 0.003 USD/liter
[5]	DCMD PTFE	Solar-driven MD; synthetic arsenic feed water with concentration 500–2000 µg/L	53 L/m^2 h with more than 99% arsenic rejection
[6]	DCMD PVDF	50 capillary membrane; lab equipment; two types of experiments: maximum concentration and long term	Arsenic in the permeate exceeded the MCL when feed reached concentration of 2000 mg/L for As (V) and 40 mg/L for As(III); Stable permeate conductivity of 3.5 µS/cm was maintained during the "long-term" experiment of 250 h; permeate flux was about 7.50 L/m^2 h
[24]	DCMD/PP and PTFE	Synthetic brackish water with 1000–10,000 mg/L TDS; 10–400 µg/L of arsenic; experiments were conducted for 12 h and for the highest arsenic, fluoride, and uranium feed concentrations	The resulting concentrations in the permeate were 0.17 µ/L, 0.56 mg/L, and 0.2 µ/L, for the three contaminants; PTFE membranes had higher fluxes compared to PP ones
[4]	DCMD PVDF	Solar-driven system; 0.0162 m^2 membrane area	100% arsenic-free water from contaminated groundwater and fluxes as high as 74 L/m^2 h.
[2]	DCMD PP and PTFE	Same experimental setup as [4]; arsenic-contaminated groundwater ranged from 0 to 1200 µg/L with pH of 7.1–7.3; the feed temperature 30–61 °C	Fluxes as high as 74 L/m^2 h and 95 L/m^2 h; 100% arsenic rejection
[16]	VMD PP/PVDF	0.018 m^2 membrane area; feed temperature 20–40 °C; synthetic arsenic-contaminated solutions feed of 1000 mg/L	No presence of arsenic detected in permeate; no need for pre-oxidation step; Fluxes of 3–12.5 L/m^2 h
[3]	VMD PTFE	Bench-scale equipment; shallow brackish groundwater of 10 g/L NaCl and arsenic concentration ranging from 0.3 to 2 mg/L	High rejection rates for both As (III) and NaCl; As (III) con in the permeate were always lower than 10 µg/L

(continued)

Table 9.2 (continued)

Ref.	MD configuration	Study synopsis	Main results
[25]	DCMD + RO PP	Integrated membrane system; part of RO permeate is directed to MD to achieve high arsenic and boron rejection; (initial concentration 9 µg/L; 0.3 mg/L)	The concentrations of arsenic and boron in the permeate of RO + MD setup are below the maximum allowable concentrations
[26]	FO-MD	Integrated FO-MD system; PVDF hollow fibers with 15 cm in length and effective area of 0.0043 m^2; 1000 ppm As (III) feed solution	High concentration of the As (III) feed solution achieved; The As (III) concentration in the MD permeate is lower than 10 µg/L
[27]	FO-MD	Feed concentration: 100–200 mg/L $NaAsO_2$, with initial As (III) concentration of 80–202 mg/L; As (V) concentration of 60–39 mg/L	High As concentration in the feed achieved; As (III) and As (V) in the permeate was below detection limit of 200 µg/L (99.9% removal)

9.3.3 *Effect of Feed Concentration on Permeability and Rejection*

In almost all the experiments by different researcher, the concentration of arsenic has little effect on the permeability, and insignificant effect on the rejection efficiency [2–5, 24, 25]. The effect of feed concentration on the permeate flux reduction is due to the reduction of vapor pressure and concentration polarization at the liquid–membrane interface. Since most of the reported experiments were conducted on relatively low feed concentrations (groundwater and/or synthesized water), the effect is expected to be minimal.

Dao et al. [3] reported that the permeate flux was the same when increasing the arsenic concentration from 0.3 to 2.0 mg/L during arsenic removal test [3]. Yarlagadda et al. [24] reported that the effect on permeate flux was minimal when the arsenic concentration was increased by 10 times the 10 µg/L MCL. A slight flux reduction of 12% was reported by Manna and Pal [5] when the arsenic concentration increased from 0 to 1200 µg/L, in the three membranes they used. The fluxes obtained for all concentrations of arsenic were almost same, leading to the negligible existence of concentration polarization [5]. A similar trend was also noticed when the arsenic concentration increased from 200 to 600 µg/L, resulting in 7% decrease of the permeate flux [4].

The effect of arsenic feed concentration on the rejection efficiency of the membrane was reported to be minimal in these studies. Qu et al. [6] found that the removal efficiencies were all higher than 99.95% and were not affected by the continuous increase of feed concentration. Manna and Pal [5] reported that no arsenic was detected in the distillate samples with more than 99% arsenic rejection. The arsenic removal efficiency and flux almost remained constant with the arsenic concentration variation and after 40 h of operation [5]. Yarlagadda et al. [24] reported that for the highest arsenic and fluoride feed concentration of 400 µg/L, and uranium feed concentrations of 30 mg/L tested, the resulting concentrations in the permeate were 0.17 µg/L, 0.56 mg/L, and 0.2 µg/L, respectively. The removal efficiency of the three contaminants for most of the tests was in the range of 99–99.9% [24].

9.3.4 Fouling and Scaling

Fouling and scaling are two important mechanisms that affect stability of the MD process and lead to reduce the overall efficiency. Despite the general statements of many MD reviews [29, 30] that membrane fouling problem is less in MD than in other membrane separations due to the relatively large pores and to the low operating pressures, the phenomena exists and contributes to membrane permeability reduction and in some cases, partial or total loss of hydrophobicity. Fouling and scaling can cause pore clogging in MD membranes which lead to reduce the membrane area available for water vaporization and hence reduces the flux [31–34]. The following paragraphs highlight some of experiences noted by several researchers during arsenic removal tests.

Scanning electron microscope (SEM) was used by Qu et al. [6] to examine PVDF membranes before and after arsenic 250-hour removal experiments. Electron micrographs showed that the morphology of the surface and inner surface had changed after the experiment. Membrane pores decreased in size and some were completely closed. However, it was reported that the membrane permeability and hydrophobicity did not changed due to morphology changes [6]. Yarlagadda et al. [24] examined a PTFE membrane before and after arsenic removal test of 12 h. The SEM scanning images did not show any characteristics of fouling, with the permeate flux remained unchanged test [24]. Manna and Pal [5] used SEM to examine PTFE membrane surface after 40 h long of arsenic removal test with feed concentration of 400 µg/L. No signs of membrane wetting or pore damages; the fluxes obtained were stable [5].

SEM analysis for the membrane sample before and after NaCl and As (III) 1000 µg/L experiment showed composition of the deposited crystal, which mainly consists of sodium and chloride [3]. The energy dispersive spectroscopy (EDS) analysis also showed a very low presence of arsenic deposits on the membrane. The deposits had a little effect on the permeate flux. To evaluate the influence of organic matter presence, long experiment of 5 days (8 h daily operation period) was conducted. In presence of organic matter, a slight decrease of permeability (5.8%) was observed as a result of fouling. However, this fouling had a negligible effect on the permeate flux and the As (III) rejection was stable at high level (more than 98.5%). The test sample consisted of 300 µg/L of As (III), 10 g/L of NaCl and 7.5 mg/L of dissolved organic carbon [3].

9.4 MD Application on Removal of Other Toxics

Membrane distillation has been utilized in removal of other toxic material. Couffin et al. [35] evaluated VMD in removing halogenated volatile organic compounds (HOVs) at low concentrations. Groundwater and surface water pollution by Volatile Organic Compounds (VOCs), particularly by halogenated VOCs (HOVs) is a common problem in industrial countries. Three compounds have been considered trichloroethylene (TCE), chloroform, and tetrachloroethylene (PCE). Activated carbon adsorption, oxidation or biological treatment are among common processes for removal of HOVs, and as stated earlier, these processes produce toxic by-products, in addition to their sensitivity for feed concentration variations. The researchers aimed at evaluating the potential. The researchers reported that technology is promising in removing HOV s at low concentration from water, particularly for the trichloroethylene, the chloroform and the tetrachloroethylene, in terms of permeate quality and high permeate fluxes achieved [35].

Bader [36] proposed a hybrid system combining liquid-phase precipitation (LPP) and membrane distillation (MD) for the treatment of the sodium-bearing liquid waste from The Idaho Nuclear Technology and Engineering facility that was established to store and reprocess spent nuclear fuel for the recovery of uranium-235. The waste stream contains nitric acid, nitrate, sodium, aluminum, potassium, sulfates, phosphates, chlorides, and toxic metals (chromium, mercury, iron, lead, nickel, and manganese); in addition to small amounts of transuranic waste known as TRU (plutonium, neptunium, americium, and curium). The integrated system consists of three main processing stages. The first stage targets the removal and recovery of nitric acid using VMD. The second stage targets mainly the removal of TRU elements along with aluminum and some toxic metals using LPP. The third stage uses MD to concentrate sodium nitrate to near saturation; and a single-stage rear-end LPP to induce the precipitation and removal of sodium nitrate from the aqueous phase. The process is claimed to provide a so-called “full separation” approach [36].

Chromium (VI) removal was a subject of study by Bhattacharya et al. [37] utilizing DCMD module with a PTFE membrane. Simulated water had concentration of feed ranging from 200 to 2000 μg/L. The researchers reported that the removal chromium (VI) through DCMD process was “exceedingly well towards the generation of clear water for repeated using” [37]. However, there was no reported data of the permeate water analysis despite the study included experimental and computational parts with a wide range of operation parameters.

Nghiem et al. [38] examined several technologies including electrocoagulation, nanofiltration (NF), membrane distillation (MD), and ion exchange resin for clean water extraction from landfill leachate. Landfill leachate contains heavy metals, pharmaceutically active compounds (PhACs), and other complex organic chemicals. The sample used by the researchers contains the following heavy metals: arsenic (215 μg/L), chromium (185 μg/L), copper (12 μg/L), nickel (75 μg/L), lead (2 μg/L), selenium (45 μg/L), zinc (124 μg/L), in addition to silver, cadmium and mercury of concentrations less than 1 μg/L. MD experiments were conducted using a closed-loop bench-scale direct contact membrane distillation (DCMD) system, with membrane cell made of acrylic plastic. Flat sheet membrane made of PTFE with (PP) support was used. Membrane pore size and porosity of the membrane were 0.22 μm and 70%, respectively. The experimental procedure consisted of 12 L of raw landfill leachate pretreated with electrocoagulation to obtain 10 L of supernatant. The effluent then was treated by NF (recovery of 70%). The resulted 7 L of permeate was then further treated with ion exchange resins for ammonia recovery, while the concentrate was treated with MD with a water recovery of 67%. The overall recovery was 90%.

The results reported by the researcher shows that NF process was also effective for the removal of PhACs to some extent with removal rate of 67% for sulfamethoxazole and 97%, triclosan after NF stage. No PhACs were detected after the MD stage. For the heavy metals, NF was successful in achieving the following removal percentages and permeate concentrations: arsenic (87%; 22 μg/L), chromium (76%; 48 μg/L), copper (90%; 8 μg/L), nickel (97%; 2 μg/L), lead (67%; 1 μg/L), selenium (32%; 35 μg/L), and zinc (90%; 14 μg/L). The NF concentrate (brine) which used as a feed for MD contained the following concentrations: arsenic (196 μg/L), chromium (436 μg/L), copper (156 μg/L), nickel (221 μg/L), lead (5 μg/L), selenium (41 μg/L), and zinc (410 μg/L). The researcher reported that all these heavy metals were not detected in the MD permeate (below detection limit of 1 μg/L) [38].

9.5 Concluding Remarks

MD technology may be considered a promising technology in providing arsenic-free drinking water. The technology has several advantages regarding the removal efficiencies and insensitivity to varying contaminated solutions. The adaptability of the technology to be utilized with different energy sources and/or integration in poly-generation systems where different services can be generated makes it attractive for applications in rural area where it is mostly needed.

Despite these advantages, all the available data comes from lab-scale and benchmark units and there is no real-life installation of MD system to treat arsenic. The questions of technology maturity and cost are the two main barriers for its realization.

Future research into arsenic removal or remediation in general needs to adapt hybrid systems where higher separation efficiency is achieved in combination with fewer drawbacks, such hazardous by-products.

Most of the available high-performance technologies such as membrane technologies and hybrid systems are relatively expensive and/or require significant investment, which is the major challenge facing rural communities in South and Southeast Asia. Therefore, research on small-scale point of use technologies that achieve safe drinking water at low cost is crucial. Another research area within such scope would be the integration of several needed services (e.g., water and electricity) which are needed in such communities and would help reduce the cost of producing safe drinking water.

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Chapter 10
Municipal Wastewater Treatment by Membrane Bioreactors

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Abstract While the population and therefore the demand for water keep increasing alarmingly, the type and quantity of water source remains the same. This leads the world to water scarcity. In this chapter, the need for wastewater recycling and stringent rules to control water pollution, instigated by water scarcity, is identified as the main driving force for the current and future increase in the use of advanced wastewater treatment systems. The types and sources of wastewater, water pollution, and pollutants along with the available treatment technologies are described. The need to continue to develop new strategies for water management is recommended. In most scenarios water reuse and/or recycling are deemed to be financially feasible approaches and hence are discussed as vital in this chapter. Municipal wastewater represents a large volume of wastewater released from different sources. The wastewater is rich in organic and inorganic compounds with high biodegradability. This chapter discusses Membrane Bioreactor (MBR) process with a special focus on biomass-based MBRs and its suitability for municipal wastewater treatment/reclamation in comparison with the existing conventional treatment technologies. Selected groups of microbes isolated and described in the literature as efficient for use in MBR systems are highlighted. The effort, desire, and market trends on MBR for municipal/domestic wastewater treatment and valorization are commentated by reviewing a wide range of projects funded by EU and other reports. It is also noted that, although there is progressive development and significant rise in the use of MBRs, severe membrane fouling and presence and retention of emerging micropollutants limited its further success. Remark is given to the importance of integrating MBR with emerging membrane operations and the simultaneous use of enzyme membrane reactors and mixed community of microbes to reclaim municipal wastewater with a desirable quality.

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Keywords Emerging micropollutants • Microbial degradation • Municipal wastewater • Membrane bioreactor (MBR) • Wastewater treatment • Water scarcity

10.1 Introduction

Among the most critical challenges facing the global society currently, is the failure to maintain and improve environmental quality or inability to achieve sustainable development. Although the capacity of the human race to overcome challenges is limitless, unpredictable disasters may occur if we fail to detect and treat existing contaminants and prevent new pollution (e.g., pollution arising from waste products of engineered nanomaterials). A substantial degradation of the environmental quality in general and water bodies in particular has been reported over the past two decades pursuant to intense anthropogenic impacts and pollution [1, 2].

The water bodies are the largest part of the environment at risk. Several factors such as inefficient use of water, contamination of water resources, improper management of water and wastewater, climate change and population growth believed to lead to water security crisis [3].

There are millions of people all over the world who have no access to water, or, if they have access, that water is unable to be used. Three quarters of the land is covered with water, however, less than 3 % is fresh water in type. Much of the fresh water is locked in glaciers and snowfields making the accessible portion of our freshwater very small. This means, only about 0.007% of the planet's water is available to serve its ever-increasing population. Hence, clean drinking water is scarce and there are millions of people across this globe that spends their entire day searching for it. Unfortunately, people who have access to safe, clean drinking water use/misuse unwisely. Moreover, worldwide, 54% of the annual available freshwater is being used. If consumption per person remains steady, by 2025 we could be using 70% of the total as a result of population growth alone [4, 5]. Fresh water is consumed daily for many purposes. The three largest consuming sectors worldwide are agriculture, industry, and domestic use [6].

In the last century the global population and so the world demand for water increased four- and sevenfold respectively [7]. Pressure on fresh water source and severe water pollution is also intensified by sudden urbanization, fast industrialization, and population expansion. Hence, domestic, agriculture, industry, and energy demands on water resources will continue to grow accordingly [4]. Freshwater pollution is majorly attributed to generation of a huge volume of toxic wastes and dumping of waste effluents. While the population and therefore the demand for water keep increasing alarmingly, the type and quantity of water source remains the same. This leads the world to water scarcity. According to the estimation by the World Water Council, 3.9 billion people will live in regions characterized as 'water scarce' by 2030 [8].

All these facts support the hypothesis that water use and demand can be affected by the changes in the demographic variables of a country's population, i.e., changes in the size, growth, structure, and distribution of a population. The impact of these demographic variables on water resources depends on the specific lifestyle of the population. The lifestyle of the population in the current epochs is changing towards consuming more water for different purposes and producing huge amount of wastewater. The huge amount of wastewater ultimately joins the water bodies in the form of pollution unless preceded by proper treatment. The phenomena of water demand increases due to several factors and potential decrease of water supply leading to water stress or scarcity is depicted in the conceptual framework in Fig. 10.1. The ever-increasing demand of water and huge production of wastewater obviously challenge the conventional treatment technologies available for water treatment. Therefore, while improving the efficiency of water use is crucial, it is equally important to integrate systems that can be used for treating wastewater and bringing it back to the water cycle as near to consumption as possible. This situation calls for recycling as much wastewater as possible.

Apart from the increased pressure on water resource, other driving forces for water recovery and recycling include the presence of rigorous environmental regulations. Reuse of wastewater conserves the supply of freshwater, thus short-circuiting the natural water cycle and presenting advantages with respect to environmental protection. More pragmatically, wastewater reuse may result directly from legislation, which prohibits the direct discharge of polluted water by making this option grueling or else bans such discharges altogether, or it may simply be favored economically regardless of regulatory stipulation. Moreover, the presence of micropollutants in wastewater treatment plant effluents has caused adverse effects in the environment, in particular with regard to fish health [1, 2, 9]. Therefore

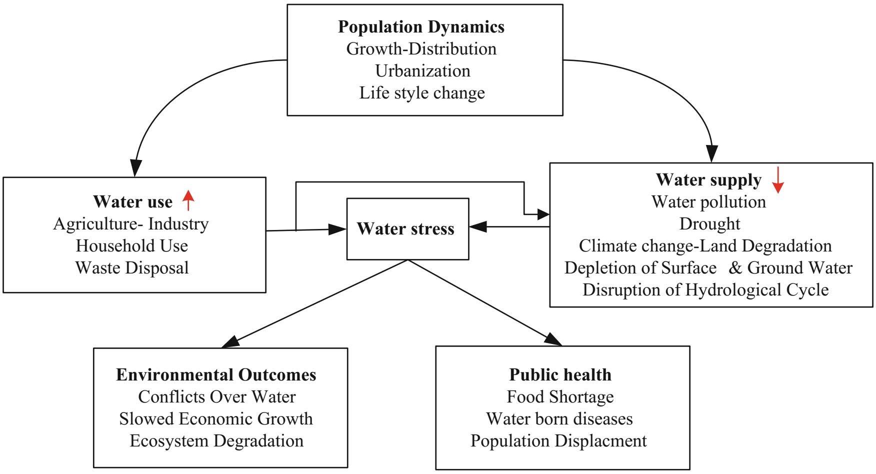

Fig. 10.1 Schematic representation of future water demand increase and water supply potential decrease leading to water stress due to human related factors and 'water stress' leading to two interrelated problems (environmental degradation and human health problems)

treating the wastewater before leaving the site where it has been generated, should become necessary for several reasons.

When dealing with water-related problems, it is important to understand the type of water-stress a certain region is suffering from. Water scarcity can be expressed as physical water scarcity and economic water scarcity. Physical water scarcity is defined as a situation where demand for water supply cannot be achieved by natural water resources due to lack of sources. Whereas economic water scarcity can be due to improper or unwise water resources management. Natural water scarcity can be due to the natural phenomena in which most of the water resources in a region are of saline sources, which are not readily available for use without prior modifications. It can also be due to drought or desertification. Figure 10.2 shows the distribution of this physical and economic water scarcity levels around the globe. For the areas where physical water scarcity is dominant, the solution should be desalination of saline water to increase the source of accessible and available water.

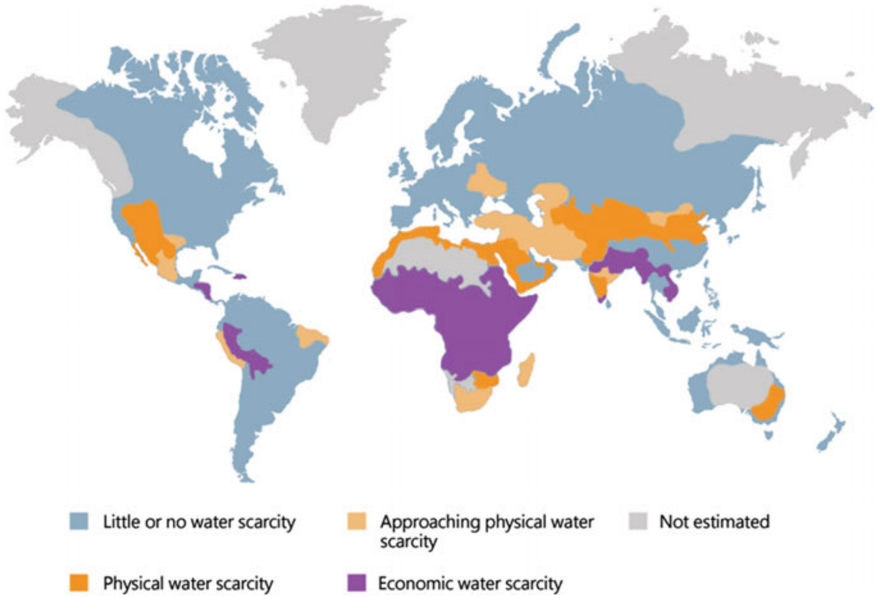

Fig. 10.2 Physical and economical water scarcity status around the globe. Reprinted with the permission from Ref. [10]. Copyright 2008 Springer Science+Business Media (**Physical water scarcity**: water resources development is approaching or has exceeded sustainable limits. More than 75% of the river flows are withdrawn for agriculture, industry, and domestic purposes [accounting for recycling of return flows]. This definition-relating water availability to water demand-implies that dry areas are not necessarily water scarce. **Approaching physical water scarcity**: More than 60% of river flows are withdrawn. These basins will experience physical water scarcity in the near future. **Economic water scarcity**: human, institutional, and financial capital limit access to water even though water in nature is available locally to meet human demands. Water resources are abundant relative to water use, with less than 25% of water from rivers withdrawn for human purposes, but malnutrition exists. **Little or no water scarcity**: Abundant water resources relative to use, with less than 25% of water from rivers withdrawn for human purposes)

Desalination is reported in other chapters of this book. The solutions related to water pollution problems are discussed in this chapter in more detail. Broadly higher productivity for water can be achieved by practicing sound measures including generating less waste, reducing water pollution, increasing reusing and recycling of water, developing effective management strategies in every aspect and sector of water use. This consequentially will help to minimize water scarcity.

10.1.1 Water Quality and Public Health

In addition to overall water shortage, poor water quality is another problem in many parts of the world. According to the World Health Organization (WHO), 1.1 billion people lack access to improved drinking water and 2.6 billion lack access to proper sanitation [11]. As many as 2.2 million people die of diarrheal related disease every year most often caused by waterborne infections, and the majority of these cases are children under the age of 5 [8]. More than ever, existing fresh water resources need protection and new water resources must be developed in order to meet the world's growing demand for clean water to safeguard public health. This will require better water treatment technologies.

10.2 Wastewater and Water Pollution

Pollution of water is a huge problem that aggravates the scarcity of water. In areas where the receiving ends are water bodies and in areas that do not necessarily have a good sewage system, water pollution is largely due to wastewater effluent. In this section, we discuss the different types of wastewater and their characterization and the major pollutants that can pollute water to make it unsafe for human use and therefore need treatment.

Characterization of waste streams from different sources is a pivotal step in designing a suitable and sustainable water or wastewater treatment technology. Characterization will help to determine the composition of waste types, their nature and the type of contaminants dominating the waste stream. If they are organics ready for biodegradation or non-biodegradables that need a different approach; if they are toxic that need special advanced systems; if they are contaminants that stay in the environment longer with a risk of bioaccumulation and bioconcentration. Based on the type of waste constituent it will be easier to plan for the appropriate technology.

10.2.1 Municipal Wastewater

The amount and type of wastewater and pollutants from municipality varies from country to country. This is due to the variation in climate, socioeconomic factors, household technology, and other factors [12]. Although it very much depends on the type of social make up generating it, municipal wastewater is mainly comprised of water together with suspended and dissolved organic and inorganic solids. Among the organic substances present in sewage are carbohydrates, lignin, fats, soaps, synthetic detergents, proteins and their decomposition products, as well as various natural and synthetic organic chemicals. Table 10.1 depicts an example for the levels of the major constituents of municipal wastewater. Municipal wastewater also contains a variety of inorganic substances from domestic and industrial sources, including a number of potentially toxic elements such as arsenic, cadmium, chromium, copper, lead, mercury, zinc, etc. [12]. Even if toxic materials are not present in concentrations likely to affect humans, they might well be at phytotoxic levels when for example are mixed with industrial effluents, which would limit their agricultural use [13, 14]. However, the type and concentration of contaminants in municipal wastewater is dependent on the source feeding the municipal sewer system.

Pathogenic viruses, bacteria, protozoa, and helminths may also be present in raw municipal wastewater and will survive in the environment for long periods. Pathogenic bacteria will be present in wastewater at much lower levels than the coliform group of bacteria, which are much easier to identify and enumerate (as total coliforms/100 ml).

10.2.1.1 Industrial Wastewater

In some areas, the wastewater from industries is strictly treated separately on site while in other areas it mingles with municipal wastewater to be treated together with domestic wastewater. Water in an industrial production is used in many process units with 50% of it taken from tap water, ground and surface water.

Table 10.1 Major constituents of typical municipal wastewater [15, 16]

Constituent	Average
Total solids	750
Dissolved solids (TDS)	533
Suspended solids	217
Nitrogen-N	48
Phosphorus-P	12
Chloride	60
Alkalinity (as $CaCO_3$)	117
Grease	100
BOD_5^2	200

Greater than half of the utilized water is eventually released as wastewater that requires an end-of-pipe treatment to meet discharge limits or to reclaim the wastewater for use [14]. The wastewater from industries varies so greatly in both flow and pollution load. It is thus impossible to assign fixed values to their constituents. Characterization of the waste stream during treatment planning is therefore essential. In general, industrial wastewaters may contain suspended, colloidal, and dissolved (mineral and organic) solids. In addition, they may be either excessively acid or alkaline and may contain high or low concentrations of colored matter. These wastes may contain inert, organic, or toxic materials and possibly pathogenic bacteria. These wastes may be discharged into the sewer system provided they have no adverse effect on treatment efficiency or undesirable effects on the sewer system. It may be necessary to pretreat the wastes prior to release to the municipal system or it might be necessary to fully treat in order to reclaim the wastewater or to discharge it directly to surface or ground waters so that it joins the water cycle again. Table 10.2, depicts the numerous types of industrial wastewater with their corresponding pollution load that they exert on treatment facilities. Among the many types of industrial wastewaters, food-processing industries contribute significantly both in terms of quality and quantity with an annual release of 500 million m^3 [14]. The food processing wastewater includes wastewaters from cheese production, milk bottling, fisheries and slaughterhouses, potato processing, beet sugar processing, tomato processing, oil extraction, fruit juice clarification, winery, etc. In most cases they constitute high organic substance that are characterized by low biodegradability and therefore requiring high biomass concentrations and hydraulic retention times to be treated in conventional activated sludge system.

10.2.1.2 Healthcare Wastewater

Healthcare/hospital wastewaters contain a variety of toxic or persistent substances such as pharmaceuticals, radionuclides, solvents, and disinfectants for medical purposes in a wide range of concentrations due to laboratory and research activities or medicine excretion. Most of these compounds belong to the so-called emerging contaminants. Emerging contaminants are quite often unregulated pollutants which may be candidates for future regulation depending on research on their potential health effects and monitoring of their occurrence. They include surfactants, pharmaceuticals and personal care products, endocrine disruptors, illicit drugs, gasoline additives, and many other groups of compounds. Their main characteristic is that they do not need to persist in the environment to cause negative effects since their high transformation/removal rates can be compensated by their continuous introduction into the environment. The quantity of wastewater produced in a hospital depends on different factors: bed numbers, hospital age, accessibility to water, general services present inside the structure (kitchen, laundry and air conditioning), number and type of wards and units, institution management policies and awareness in managing the structure in safeguarding the environment, climate and cultural and geographical factors. The daily water consumption rates in healthcare facilities are

Table 10.2 Pollution strength of effluents from various industries [17]

Type of waste	BOD_5 (mg/l)	COD (mg/l)	SS (mg/l)	pH
Clothing				
Cotton	200–1000	400–1800	200	8–12
Wool scouring	2000–5000	2000–5000	3000–30,000	9–11
Wool composite	1	–	100	9–10
Tannery	1000–2000	2000–4000	2000–3000	11–12
Laundry	1600	2700	250–500	8–9
Food				
Brewery	850	1700	90	4–8
Distillery	7	10	Low	–
Dairy	600–1000	–	200–400	Acid
Cannery				
Citrus	2000	–	7000	Acid
Pea	570	–	130	Acid
Slaughterhouse	1500–2500	–	800	7
Potato processing	2000	3500	2500	11–13
Sugar beet	450–2000	600–3000	800–1500	7–8
Farm	1000–2000	–	450–800	7.5–8.5
Poultry	500–800	600–1050		6.5–9
Materials				
Pulp: sulfite	1400–1700	–	Variable	
Pulp: kraft	100–350	170–600	75–300	7–9.5
Paperboard	100–450	300–1400	40–100	
Strawboard	950	–	1350	
Coke oven	780	1650	70	7–11
Oil refinery	100–500	150–800	130–600	2–6

spread between 200 and 1200 L/bed with the highest values coming from industrialized countries and the lowest ones from developing countries. Referring to the presence of macro- and emerging micro-contaminants, healthcare wastewater has two to three times more BOD_5, COD and SS as compared to municipal wastewater [18].

10.2.2 Water Contaminants/Pollutants

10.2.2.1 Common Macro-pollutants

Conventional pollutants of wastewater or parameters to determine pollution from various sources includes BOD_5, COD, and SS. Taking the corresponding average values for BOD_5, COD, and SS, the wastewaters' pollution strength is classified as low, medium, or high strength.

Dissolved oxygen is a key element in water quality. A demand is placed on the natural supply of dissolved oxygen by many pollutants in wastewater. This is called biochemical oxygen demand, or BOD, and is also used to measure the efficiency of wastewater treatment plant. If the effluent, the treated wastewater produced by a treatment plant, has a high content of organic pollutants or ammonia, it will demand more oxygen from the receiving water and leave the water with less oxygen to support fish and other aquatic life. The organic matters are 'oxygen-demanding' substances. Oxygen-demanding substances can be contributed by domestic, agricultural and industrial wastes, such as those from food processing, paper mills, tanning, and other manufacturing processes. These substances are usually destroyed or converted to other compounds by bacteria if there is sufficient oxygen present in the water, but the dissolved oxygen needed to sustain aquatic life is used up in this process, which subsequently leads to waterbody eutrophication adding up to the existing water scarcity.

Pathogens

Disinfection of wastewater and chlorination of drinking water supplies has reduced the occurrence of waterborne diseases such as typhoid fever, cholera, and dysentery, which remain problems in underdeveloped countries while they have been almost eradicated in developed nations. Pathogens may be carried into surface and groundwater by wastewater from residential areas and institutions, by certain kinds of industrial wastes and by storm runoff pollution. Humans may come in contact with these pathogens either by drinking contaminated water or through swimming, or other contact activities.

Nutrients

Carbon, nitrogen, and phosphorus are essential to living organisms and are the chief nutrients present in natural water. Large amounts of these nutrients are also present in sewage, certain industrial wastes, and drainage from fertilized land. Conventional secondary biological treatment processes do not remove the phosphorus and nitrogen to any substantial extent. Indeed, they may convert the organic forms of these substances into mineral form, making them more usable by plant life. When an excess of these nutrients overstimulates the growth of water plants, the result causes unsightly conditions, interferes with drinking water/wastewater treatment processes, and causes unpleasant and disagreeable tastes and odors. The release of large amounts of nutrients, primarily phosphorus but occasionally nitrogen, causes nutrient enrichment which results in excessive growth of algae. Uncontrolled growth of algae shades and prevents sunlight penetration into the waterbody during day time making life difficult for smaller aquatic plants and depletes dissolved oxygen in the water at night affecting aquatic animals. The release of excess amount of nutrients than needed by the affected waterbody results in eutrophication which is a condition resembling nutrient enrichment.

Inorganic and Synthetic Organic Chemicals

A variety of chemicals can be listed in this group including detergents, household cleaning aids, heavy metals, pharmaceuticals, synthetic organic pesticides and herbicides, industrial chemicals, and the wastes from their manufacture. Many of these substances are toxic to aquatic life and many are harmful to humans. Some are known to be highly poisonous at very low concentrations. Others can cause taste and odor problems, and many are not effectively removed by conventional wastewater treatment mechanisms.

10.2.2.2 MicroPollutants (Emerging Recalcitrant Contaminants)

The term 'micropollutants' means organic or mineral substances whose toxic, persistent, and bioaccumulative properties may have a negative effect on the environment and/or organisms. Such pollutants are most common in wastewater coming from such as healthcare facilities. A great variety of chemical substances are commonly used in hospitals for laboratory and research activities. These include pharmaceuticals, diagnostic utilities, and disinfectants [18].

Most contaminants which are recalcitrant in nature are xenobiotic compounds. These compounds are not commonly produced by nature. However, unfortunately, they are part of human life in the modern society. Different industries develop and produce various compounds that should improve human's life. However, most of them are highly toxic to the environment if not managed properly. Most of the xenobiotic compounds are nondegradable in nature; they are recalcitrant by property which means they exhibit the following properties:

- Non-recognizable as substrate by microbes to act upon and degrade it.
- They do not contain permease (membrane transport proteins) which is needed for transport into microbial cell.
- Large molecular nature that complicates its entry to microbial cell.
- They are highly stable (they are insoluble in water, the general solvent, attributing to their stability).
- They are mostly intrinsically toxic.

The recalcitrant xenobiotic can include the following groups based on their compositions:

Halocarbons: They consist of halogen group in their structure. Mainly used in solvents, pesticides, propellants, etc. They are highly volatile and are present in insecticides, pesticides, etc.

Polychlorinated biphenyls (PCBs): They consist of a halogen group and benzene ring. They are mixtures of synthetic organic chemicals. They are chemically inert and characteristically hydrophobic organic contaminants. Due to their non-flammability, chemical stability, high boiling point, and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics, and rubber products; in pigments, dyes, and carbonless copy paper; and many other applications. Therefore, PCBs are toxic compounds that could act as endocrine disrupters and cause cancer.

Synthetic polymers: These are mainly used to form plastics like polyester, polyvinyl chloride, etc. They are insoluble in water and of high molecular weight.

Alkylbenzyl Sulphonates: They consist of a sulphonate group which resists breakdown by microbes. They are mostly found in detergents.

Oil mixtures: When oil spills occur covering a huge area, the breakdown by action of microbes becomes non-effective.

Artificial hormones: The presence of such micropollutants in wastewater treatment plant effluents has been causing adverse effects in the environment [1, 2, 9]. Among these, human estrogens (mainly estradiol E2 and estrone E1) and the artificial estrogen ethinylestradiol (EE2) are responsible for a significant part of the endocrine disrupting effects seen in the aquatic organisms [19, 20].

Other recalcitrant contaminants: A number of pesticides are based on aliphatic, cyclic ring structures containing substitution of nitro-, sulphonate, methoxy-, amino and carbomyl groups; in addition, they also contain halogens. These substitutions make them share the properties of recalcitrant contaminants.

10.3 Water Treatment

Our world currently faces a global water challenge. More than ever, existing fresh water resources need protection and new water resources must be developed in order to meet the world's growing demand for clean water. Studies tend to support the view that treating water can reduce diarrheal incidence by about 20% [21]. The transmission of faeco-oral diseases is interrupted primarily by improved water supply and improved hygiene [22]. Drinking water disinfection has remarkably contributed to the reduction in world mortality and morbidity figures in the past [23]. It has been able to eliminate life-threatening disease such as cholera and typhoid. Drinking water disinfection has been done through water treatment processes including settlement, coagulation, and filtration or through chemical treatment processes, such as chlorination or ozonation.

Available water treatment technologies include preliminary/primary water treatment processes (screening/grit chambers, sedimentation tanks, and biological treatment) aiming at the physical contaminants, secondary treatment processes (biofiltration, activated sludge process, trickling filters, and oxidation ponds) and tertiary/advanced water treatment process including ion exchange and advanced oxidation systems like ozonation, UV radiation, electrocatalytic processes, and electro-fenton oxidation, etc. The secondary treatment processes generally target the biodegradable content of the waste stream. Constructed wetlands/natural wetland systems or lagoons, for instance, in warmer climates, make use of natural resources by allowing the wastewater to be retained in the ponds for about two to three weeks; the organic contaminants will undergo bacterial decomposition. The algal community can use the CO_2, ammonia and nitrate produced from the process while the organic sludge sediments at the bottom of the pond to finally release methane as energy. The problem related to these systems is the need for warmer temperature and the potential of being a suitable habitat for insect vectors.

Figure 10.3 summarizes the general flow of processes for a typical conventional treatment of municipal wastewater. The major disadvantages associated with conventional wastewater treatment practices are

- Generation of large amounts of sludge that requires an off-site disposal that incurs the largest single-cost component in operating wastewater treatment plant.
- Most wastewater treatment processes are affected by diurnal or seasonal influent quality.
- Their high energy requirement makes them unsuitable for low per-capita energy consumption countries.
- Requires a number of operations and maintenance routines.

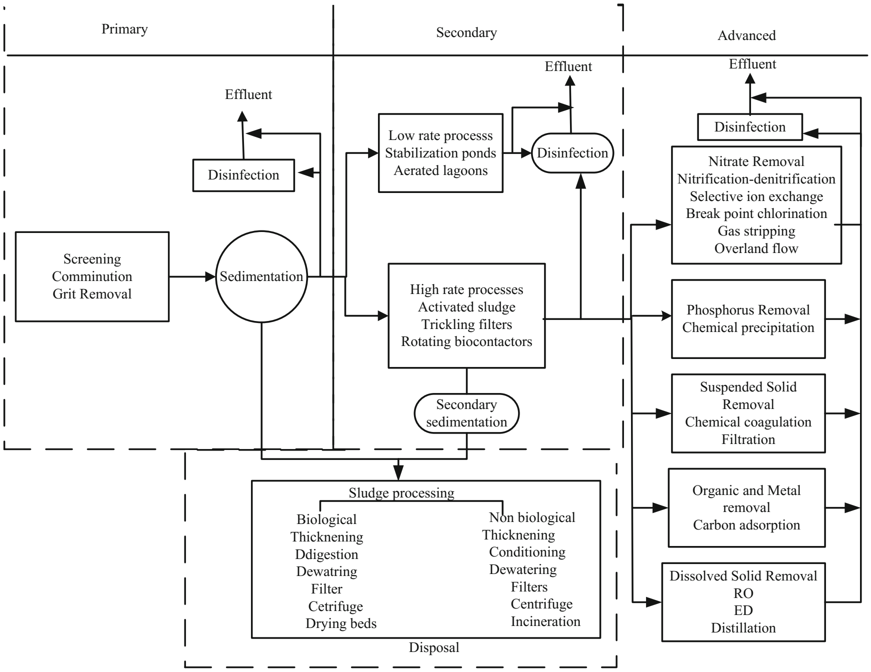

Fig. 10.3 A summarized flow chart of conventional municipal wastewater treatment process adapted from Asano [16] with kind permission from Springer Science+Business Media

10.3.1 Membrane Technology

Membrane processes during water treatment are designed to carry out physical or physicochemical separations. The development of membrane-based bulk water and wastewater treatment processes is significant, since they offer three clear advantages over conventional techniques

(a) Separation is achieved without requiring a phase change, and is therefore more energetically efficient than distillation.
(b) It is operated continuously under steady-state condition without necessitating regeneration cycles, unlike adsorptive separation processes.
(c) Little or no chemical addition is required, unlike conventional clarification which generally relies on the addition of chemical coagulants and flocculants, hence limited sludge production.

Membrane technology is currently being used to enhance conventional water treatment technologies with microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) as the most widely used. These technologies are applied as standalone, sequentially integrated with one another or in hybrid with conventional treatment mechanisms [14]. Membranes are favored over other technologies for water treatment, such as disinfection, distillation, or media filtration due to the three main reasons listed. Typically, pressure-driven membranes are classified according to characteristic pore size or their intended application. Currently, membrane technology is commercially available for suspended solids, protozoa, and bacteria removal (MF), for virus and colloid removal (UF), for hardness, heavy metals, and dissolved organic matter removal (NF), and for desalination, water reuse, and ultrapure water production (RO) [24]. As we move forward, continued research efforts and materials development shall ensure that membrane technology will help to protect our environmental resources and produce clean water in an energy efficient manner to alleviate the problem of water scarcity.

10.3.1.1 Microfiltration (MF)

MF membranes which usually hold 0.1–10 μm pore sizes serve for the separation of solutes at a low pressure difference within 2 bar [25]. As a result it is mainly used to remove courser particles and suspended solids. For instance, during olive mill wastewater treatment, MF helps to remove dissolved organic pollutants and other soluble large-size contaminants [26, 27]. MF is mostly used as a pretreatment in integrated/hybrid systems to remove the suspended particulate matter present in wastewater. Pretreatment by MF prior to other membrane operations is often observed to provide superior performance compared to conventional pretreatment strategies [28]. In some cases MF can also be used as a posttreatment step while treating municipal or industrial effluents.

10.3.1.2 Ultrafiltration (UF)

Ultrafiltration is a membrane separation process, mostly used in the separation of macromolecules and colloids from a solution [25]. Retained solutes usually have molecular weights of a few thousand Daltons. It is greatly successful in removing contaminants present in wastewaters discharged from municipal wastewater as well as various chemical, pharmaceutical and food industries [29–31]. Although the water reclaimed through UF is not qualified for applications in primary processes that requires consistent clean or softened water, it can be reused in subsidiary industrial processes such as rinsing and washing. UF is usually employed as a pretreatment in systems requiring highly purified water often followed by NF or RO to achieve the desired water quality [32].

10.3.1.3 Nanofiltration (NF)

Nanofiltration membrane process is characteristically situated between UF and RO. It is popular as an effective yet simplified water treatment mechanism attributed to the various benefits it offers in terms of environmental pollution abatement, rejection, recovery, and reuse of important components, auxiliary chemicals, recovery, and reuse of brine. Additionally, the production of quality permeate allows the reuse of treated waters in major processes [33]. Governed mostly by steric and Donnan exclusion, it is able to completely retain multivalent ions thus resulting in high solute selectivity. Moreover, NF has high solvent permeability and the ability to reject dissolved uncharged solutes such as organic molecules, with molecular weight greater than 150 Da. For instance, NF has been demonstrated to be a promising alternative for eliminating pharmaceuticals considered as emerging recalcitrant with greater than 90% removal efficiency [34].

10.3.1.4 Reverse Osmosis (RO)

RO is effective in removing macromolecules as well as ions from wastewater. RO permeate is free from color compounds and has low total salinity [35]. For instance, several studies described the effectiveness of RO in the removal of contaminants like pharmaceuticals and endocrine disrupter compounds from drinking water. Both NF and RO showed excellent overall performance with high rejection percentages for almost all of the pharmaceuticals investigated (>85%) [36]. In another study, RO was also able to remove all the investigated compounds below their corresponding detection limits, including those that were not significantly removed at sludge residence time of 30 days (for instance, galaxolide) using conventional activated systems (CAS) or media filtration [37, 38].

While pressure-driven membranes processes perform well in many applications, the drive to protect existing water resources and to produce new water resources demands membranes with improved productivity, selectivity, fouling resistance, and stability that is available at a reasonable cost. Better membrane process requires better process design, maintenance, and operation and fouling control for longer life span.

10.3.2 Membrane Bioreactor (MBR)

Pressure-driven membrane processes ranging from MF to RO are good enough to produce clean water out of wastewater. However, membrane process suffers from process limitations. The two main limitations are membrane fouling and retention of small molecules. Due to these limitations membrane processes require further integration with conventional treatment systems such as bioreactors. Integration of membrane process with bioreactors brings about a significant degradation of organic fractions of the wastewater.

Biomass-based MBR process is a very compact arrangement that combines a suspended growth-activated sludge system with microporous membranes. It is a reliable and efficient technology that has become a legitimate alternative to conventional activated sludge processes for many domestic and industrial applications. It has been successfully applied at an ever-increasing number in all parts of the world. Generally, biomass-based MBRs are considered as an advanced form of conventional wastewater treatment process that eliminates one or more of the principal limitations of conventional activated sludge. The membrane bioreactor (MBR) process uses a microfiltration (MF) or ultrafiltration (UF) membrane to perform the solid–liquid separation and combines activated sludge, 1° and 2° clarification, filtration and MF/UF into one unit operation-bioreaction (Fig. 10.4). The figure illustrates how MBR with a submerged membrane configuration compacts the foot print of the wastewater treatment process as a process intensification of activated sludge system.

The membrane process is used for solid/liquid separation in the place of secondary clarifiers. It allows the complete physical retention of bacterial flocs and all suspended solids within the bioreactor. As such it has demonstrated many advantages over conventional wastewater treatment processes including: small footprint and reactor requirements, high effluent quality, good disinfection capability, higher volumetric loading, and less sludge production [39]. In particular, complete retention of microorganisms as well as some dissolved organic matter by the membrane process resolves the multistage downstream/posttreatment required in conventional biological treatment systems. The effluent water with less than 1 mg/L SS, 0.2 NTU turbidity and up to 4 log virus removal is suitable for reuse or as feed water source for RO treatment. Therefore, with the current focus on wastewater reclamation and water reuse, MBR has now become an attractive option for the treatment and reuse of industrial and municipal wastewaters. BCC research reported that the total cost of a MBRs increased to $425.7 million in 2014 from $375 million in 2010 [40] and is estimated to be around $778 million by 2019. Currently, there are a large number of plants with a treatment capacity of around 5–

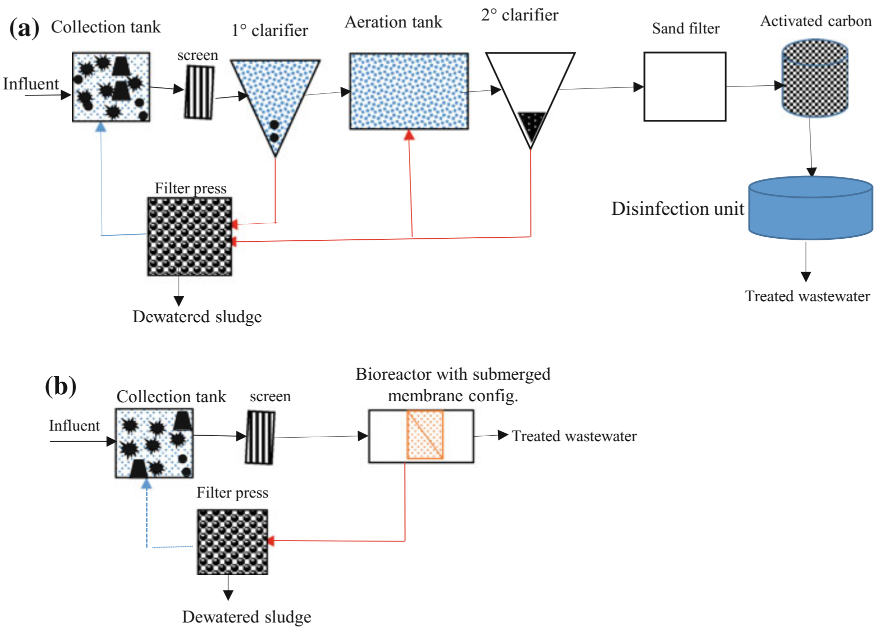

Fig. 10.4 Schematic process flow of municipal wastewater treatment by **a** conventional activated sludge system and **b** MBR with submerged membrane configuration

10 mega liter per day (ML/d) while the next generations of MBRs are being designed with capacities up to 45 ML/d.

The need to combat the issue of water scarcity and sustainability requires the development of new strategies for water management and water reuse schemes. MBRs are therefore shown to be technically and financially viable to address the urge for water recycle and reclamation. Promising areas of application are municipal wastewater, food-processing wastewater, slaughterhouse wastewater, and landfill leachates treatments. Another promising area of MBR application is in the removal of nitrate in drinking water since it has many advantages over traditional biological denitrification [41].

10.3.2.1 Types of Membrane Bioreactor Configurations

Based on the membrane module configuration, MBRs can be classified into side-stream or submerged/immersed MBR system (Fig. 10.5). In side-stream membrane reactors (sMBR) where the membrane module is placed externally to the reaction mixture, separation is carried out by pressure-driven filtration. Whereas in submerged/immersed MBR (iMBR) system, separation is carried out by vacuum-driven membranes immersed directly into the bioreactor, which operates in dead-end mode. The sMBR process has an advantage of operating at relatively high

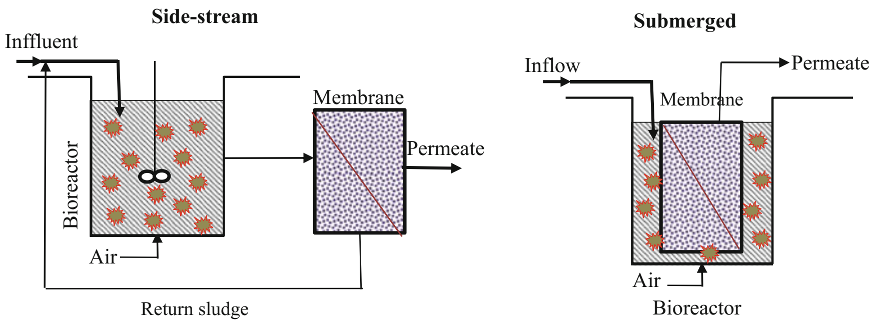

Fig. 10.5 Schematic classification of MBR based on membrane module configuration; *left* side-stream MBR with external pressure-driven membrane filtration and *right* submerged MBR with internal vacuum-driven membrane filtration

membrane fluxes (with typical values ranging from 50 to 150 L/m^2 h) using a pump to provide cross-flow [42]. However, in order to maintain the required shear at the membrane surface, recirculation flows for the sMBR process are often greatly increasing its energy consumption. This might make sMBR less economical for large municipal wastewater applications compared to iMBR. In sMBR, since the permeate flux is relatively high, membrane fouling is more prevalent. Pumping of activated sludge in sMBR induces shear stress to microbial agglomerate, leading to their break-up. This in turn causes a decrease in particle size with the release of foulant material from the agglomerates which might be the reason for increased membrane fouling rate in this configuration. Moreover, the combination of the two unit operations (bioreaction and membrane filtration) into one and the ability to operate at elevated solids concentration significantly reduces the footprint in the case of the iMBR process [43, 44]. Other process parameters that differ during the two configurations compiled from various reports are crudely summarized in Table 10.3.

10.3.2.2 Microbial Degradation

The major component of municipal wastewater based on volume/volume composition is organic, which is rich in carbon content and embrace high energy. Therefore many decomposers naturally gain the capacity to explore these organic compounds as a source of carbon and energy for their biomass production. This has been known to researchers since nearly a century. Accordingly, there are many reports on the degradation of water pollutants by different microbes. Currently more than 200 genera from bacteria, cyanobacteria, algae, and fungi groups are isolated, described, and tested by various researchers in different applications [45]. The groups bacteria, cyanobacteria, microalgae, fungi, and yeasts are all considered and proved to have different level of efficiency for the degradation of conventional and emerging contaminants from waste streams.

Table 10.3 Comparison of process conditions for side-stream and submerged/immersed MBR systems

Characteristics	Side-stream	Submerged
Surface area	Low	High
Flux	High	Low
TMP	High	Low
Energy for filtration	Medium	Lower
Capital cost (Capex)	Low	Low to medium
Operational cost (Opex)	Low to medium	Low
Foot print	Medium	Small
Fouling risk	High	Low
Aeration cost	Low	High
Liquid pumping cost	High	Low
Cleaning required	Frequent	Less frequent
Maintenance	Simple	Complex

Bacteria are the main group of all in terms of biodegradation of contaminants. Several of them are known to feed exclusively on organic compounds. Biodegradation of organic compounds can occur under aerobic and/or anaerobic conditions [46]. Thus, numerous genera of aerobic and anaerobic bacteria are isolated and documented for specific types of contaminants. Among the bacteria, the Pseudomonas species are generally considered to be the best groups for efficient degradation of the xenobiotics. Bacillus species are often responsible for hydrolyzing of most xenobiotics. The pseudomonas can bring about hydrolysis as successfully as they do dehalogenation, hydroxylation, aromatic ring cleavage, and nitro-group reduction.

Bacterial strains that are able to degrade aromatic hydrocarbons have been repeatedly isolated, mainly from soil. These are usually gram-negative bacteria, most of them belonging to the genus Pseudomonas. Nevertheless, the biodegradative pathways have also been reported in bacteria from other genera including *Mycobacterium, Corynebacterium, Aeromonas, Rhodococcus, Bacillus*, etc. [47].

The biotransformation of PCBs by a variety of bacterial strains from wastewater has also been well documented. Higher chlorinated PCBs are subjected to reductive dehalogenation by anaerobic bacteria while lower chlorinated biphenyls are best oxidized by aerobic bacteria. Aerobic bacteria strains isolated for the biotransformation of higher halogenated PCBs include species belonging to the genera *Pseudomonas, Burkholderia, Ralstonia, Achromobacter, Sphingomonas, and Comamonas* [48].

Positive results are also documented on the efficiency of bacteria for the removal of several compounds of pesticides. The bacterial groups responsible for the degradation of pesticides include the *Providencia stuartii* (chlorpyrifos degrading bacterium), *Bacillus, Staphylococcus and Stenotrophomonas* (for the degradation of dichlorodiphenyltrichloroethane) [49, 50]. Other groups of pollutants degraded by bacterial groups include azo dyes (***Shewanella***/oneidensis) and heavy metals (transformation to a less toxic state: the methylation of mercury by bacillus bacteria is a good example) [51].

Even though Bacteria are the primary responsible group for the detoxification of calcitrants, other groups such as algae, fungi, and yeasts are also frequently used in the degradation or biotransformation of wastewater contaminants. Protozoa appear to be only rarely involved in the degradation application. Some genera of the different groups together with the mechanisms they are involved in are compiled from the literature as an example for the application of microbes for the degradation or transformation of pollutants and are summarized in Table 10.4.

10.3.2.3 Case Study: Municipal Wastewater Treatment

Municipal wastewater is usually treated to get rid of undesirable substances by subjecting the organic matter to biodegradation by microorganisms such as bacteria. The biodegradation involves the degradation of organic matter to smaller molecules (CO_2, NH_3, $PO_{4,}$ etc.), and requires constant supply of oxygen. Over the past two decades, for municipal wastewater that is generally high in organic fraction and volume, MBR becomes economically attractive when a compact technology is required or high effluent quality is required for reuse. The continued push towards stricter discharge standards, increased requirement for water reuse and greater than before urbanization and land limitations will further fuel the use of this technology. In some countries industrial and healthcare wastewater are also allowed to join municipal wastewater. Hence treating and reclaiming municipal wastewater using MBR can help resolve part of the water scarcity problem. The challenges will center on scale-up, ease of operation, increased energy efficiency, membrane biofouling, simplified membrane cleaning and replacement schemes, leak of emerging contaminants and peak flow management.

In particular, the process of supplying oxygen is expensive, tedious, and requires a lot of expertise and manpower. In conventional wastewater treatment systems, these problems are overcome by growing microalgae in the ponds and tanks where wastewater treatment is carried out. The algae release the O_2 while carrying out the photosynthesis which ensures a continuous supply of oxygen for biodegradation. Algae-based municipal wastewater treatment systems are mainly used for nutrient removal (removal of nitrogen and phosphorous). The added benefit is the resulting biomass that can be used as biofuel feedstock. Advantages of algal-based wastewater system over conventional system are

Cost Effectiveness: It is a more cost-efficient method to remove biochemical oxygen demand (BOD), pathogens, phosphorus and nitrogen than activated sludge process and other secondary treatment processes [56].

Low Energy Requirement: Traditional wastewater treatment processes involve the high energy costs of mechanical aeration to provide oxygen to aerobic bacteria to consume the organic compounds in the wastewater, whereas in algae-based

Table 10.4 Selected groups of microbes isolated and described in literature as efficient decomposers of organic pollutants and the major biodegradation path ways they involved in, collected and summarized from different reports [45, 52–55]

Groups	Selected genera in the group	Biodegradative pathways	Remarks
Algae	Chlorophyta	Nitro-group reduction	
	Cyanophyta	P and/or N uptake	
	Bascillariophyta	Pathogen removal	
	Euglenophyta		
Bacteria	Pseudomonas	Detoxification, hydrolysis, dehalogenation	Also aromatic ring cleavage
	Bacillus	Hydrolysis	Also hydroxylation
	Rhodococci	Dehalogenation, denitrification and phosphate removal	Able to degrade substituted and non-substituted OC
	Staphylococcus	Hydrolysis, detoxification of pesticides	
	Actinobacteria	Bioconversion of organics	
	Aeromonas	Hydrolysis	
	Klebsiella		
Cyanobacteria	Anabaena	Dehalogenation, direct uptake of nutrients	
Fungi	Aspergillus	Methylation of hydroxyl- and amino-groups and metals	Are especially good for compounds not readily degraded by bacteria
	Penicillium	Ion exchange, chelation, adsorption and active uptake	
	Phialophora	Cellulose degradation	
	Rhodosporidium		
Yeast	Pichia (*Hansenula polymorpha*)	Adsorption, oxidation	
	Candida	Oxidation of an amino group, ring cleavage	
	Yarrowia	Same like pichia	

wastewater treatment, algae provides the oxygen for aerobic bacteria through photosynthesis while consuming nutrients.

Reductions in Sludge Formation: In conventional wastewater treatment systems chemicals used for effluent treatment results in huge amounts of sludge. Whereas in algae wastewater treatment facilities, the resulting sludge with algal biomass is energy rich which can be further processed to make biofuel or other valuable products such as fertilizers.

Greenhouse Gas Emission Reduction: since algae-based wastewater treatment consumes more CO_2 while growing than it is released, the entire system carbon is negative.

Algal Biomass Production: The resulting algae biomass is a source of useful products such as biodiesel. Under controlled conditions algae are capable of producing 40 times the amount of oil for biodiesel per unit area of land, compared to terrestrial oilseed crops such as soy and canola [57].

Pathogen Removal: Algal photosynthesis increase the pH of an aqueous medium due to the simultaneous removal of CO_2 and H^+ ions and the uptake of bicarbonate when the algae are carbon limited [58, 59]. According to Rose et al. [60] a higher pH medium will provide a 100% kill of E. coli and most pathogenic bacteria and viruses.

To construct algae-based wastewater treatment system it is essential to consider both wastewater treatment as well as algal cultivation. Cell retention time, nutrient addition rate, water depth, and degree of mixing are the common parameters considered for growth of algae. In addition to these parameters BOD reduction, TDS reduction, pH, nitrogen removal rate, and phosphorus removal rate are commonly considered. Hence the system should allow the growth of algae as well as wastewater treatment.

Hence, exploiting the advantage of algae-based biomass in MBR could lead to resolving part of the limitations a conventional MBR could face in long term sustainable operation. For instance, the cost of energy required to oxygenate the system can easily be reduced by using algae since algae can produce oxygen through photosynthesis with low energy input.

Biology of Biomass-based MBRs

Biomass-based MBRs produce 20–50% less sludge than conventional systems as they operate at low food-to-microorganism (F/M) and higher sludge retention time (SRT). The size of the biomass flock formed depends on the SRT value and on the MBR configuration used. They are generally characterized by the presence of small and staggered flocks, and free bacterial cells. In addition, the low F/M ratios favored the growth of filamentous and other competitive microorganisms. Due to the conducive environment available for the growth of 'nitrifiers' and 'denitrifiers', simultaneous removal of N and dissolved N is possible [42, 44].

10.4 Existing Practices and Trends in MBR for Municipal Wastewater Treatment

The effort and desire on MBR for municipal/domestic wastewater treatment and valorization is reflected in a wide range of projects funded by EU (http://cordis.europa.eu). Some selected projects that are funded under the frameworks of FP7 and FP6 are summarized in Table 10.5 to show the area of focus by researchers regarding wastewater treatment using MBR. The projects comprise the novel use of degrading microorganisms to treat water, to prevent pollution and to restore energy in different forms. They applied selected groups of bio-degraders from aerobic bacteria to consortia of communities for maximum achievement. Most of this selected processes aimed to tackle the emerging micropollutants by applying innovative MBR in varying arrangements. The project MINOTAURUS involved a holistic application of MBR for preventing soil and groundwater pollution from micropollutants and the conversion of domestic waste water to energy. In most of the projects, the training and awareness creation for stakeholders in the form of workshops and summer schools (even MSc programs in limited number) is reported. This has an implication for the future use of the technology as more researchers will be aware; more developments and more needs will be sought. Most of the projects are under small and medium scale. Moreover the European Commission has funded the following three FP6 MBR projects that also involve research, development, capacity building and technological transfer under the FP6 program. All three FP6 projects listed in Table 10.5 that involve more than 50 European and international companies and institutions are completed and the commercialization of research outcomes could be in its way. This is contributing to the rising application of MBR as a choice for municipal waste water treatment.

10.4.1 MBR Expansion in the Market

Market trends indicate MBR technologies will be increasingly utilized as part of wastewater treatment, water reuse programs to conserve our natural water resources and to provide new water sources. It is estimated that there are about 6000 plants operating worldwide and roughly 600 plants in use in the USA (http://www.amtaorg.com/). From small, point-of-use plants to large municipal plants producing 40 million gallon per day (MGD = 1.75 m^3/s), MBR systems are now considered mainstream and widely accepted as best available treatment for municipal wastewater influent. Building on numerous system innovations, the technology is considered by many industry professionals to be ‘the treatment technology of choice’ regardless of the size or application.

10.5 Performance Limitations of MBR

10.5.1 Membrane Fouling/Biofouling

The membrane performance generally depends on the interaction between the membrane and the activated sludge as well as on the operating conditions. Activated sludge consists of suspended particles, i.e. microorganisms, colloids, and

Table 10.5 Selected EU FP7 and FP6 funded projects for the municipal/waste/water treatment using membrane bioreactor extracted from http://cordis.europa.eu using membrane process and municipal wastewater, domestic wastewater, membrane bioreactor as key words

Project acronym and title	Main aim	Project status	Project reference
BIOTREAT (Biotreatment of Drinking Water Resources Polluted By Pesticides, Pharmaceuticals and Other Micropollutants)	The overall objective of BIOTREAT was to develop new technologies for bioremediation of drinking water resources contaminated with micropollutants such as pesticides and pharmaceuticals. The technologies are based on the introduction and efficient exploitation of degrader bacteria in existing sand filters at waterworks	Completed (01/01/2011–31/12/2014)	Project reference: 266039 Funded under: FP7-KBBE
MINOTAURUS (Microorganism and enzyme Immobilization: novel techniques and approaches for upgraded remediation of underground, wastewater and soil)	The MINOTAURUS project aims to develop efficient treatment options to remove micropollutants from wastewater and to remediate groundwater and soil contamination. The investigated technologies are all based on the concept of immobilization of biocatalysts to enable an intensified biodegradation of targeted pollutants using 1. Bioaugmented membrane bioreactor for municipal and hospital wastewater treatment targeting residues of pharmaceuticals and endocrine disrupting compounds 2. packed-bed reactor for aerobic treatment of groundwater contaminated with CAHs 3. packed-bed reactor for remediation of groundwater containing Methyl tertiary-butyl ether/Tert-butyl alcohol (MTBE/TBA)	Completed (01/01/2011–31/12/2013)	Project reference: 265946 Funded under: FP7-KBBE
BIOWET (Advanced Biological Waste-to-Energy Technologies)	The IRSES “BioWET” project integrates a number of advanced biotechnologies for waste-to-energy conversion. Within this aim, at WP 2—the use of anaerobic membrane bioreactor (AnMBR) for the treatment of domestic sewage has been tested	Completed (01/01/2012–31/12/2015)	Project reference: 269255 Funded under: FP7-PEOPLE

(continued)

Table 10.5 (continued)

Project acronym and title	Main aim	Project status	Project reference
DESSIN (Demonstrate Ecosystem Services Enabling Innovation in the Water Sector)	DESSIN aims to demonstrate and promote innovative solutions for water scarcity and water quality/the implementation of the Water Framework directive (WFD), and to show the value of those solutions for the water sector and society by also developing and demonstrating a methodology for the valuation of ecosystem services (ESS) as catalyzer for innovation. Within this aim, the project focuses on the design of a packaged plant consisting of an advanced membrane bioreactor coupled with nanofiltration and reverse osmosis membranes that has been installed in KEREFYT, the Sanitary Engineering Research and Development Center of EYDAP in Greece	On progress (01/01/2014–31/12/2017)	Project reference: 619039 Funded under: FP7-ENVIRONMENT
PURATREAT (New Energy Efficient approach to the operation of Membrane Bioreactors for Decentralised Wastewater Treatment)	The main goal was to develop a method for decentralized wastewater treatment that allows the reuse of water with minimal operational and maintenance costs. This project studied the most suitable MBR wastewater technology applicable to peri-urban areas	Completed (01/01/2006–30/06/2009 Pilot MBR were built	Project reference: 15449 Funded under: FP6-INCO
AMEDEUS (Accelerate Membrane Development for Urban Sewage Purification)	The aim was tackling both issues of accelerating the development of competitive European membrane bioreactor (MBR) filtration technologies and increasing acceptance of the MBR process through decreased capital and operational costs. The project targeted the two market segments for MBR technology in Europe: the construction of small and medium-size	Completed (01/10/2005–31/05/2009)	Project reference: 18328 Funded under: FP6-SUSTDEV
EUROMBRA (MBR with an EU perspective for advanced municipal wastewater treatment strategies for the 21st century)	The main aim is to develop cost-effective, sustainable solutions for new and advanced municipal wastewater treatment based on MBR technology	Completed (01/10/2005–31/05/2009)	Project reference: 18480 Funded under: FP6-SUSTDEV

solutes. These components have a significant effect on the membrane fouling although their contribution in literature is discussed controversially. The liquid phase of the activated sludge system consists of solutes and different amounts of colloids, i.e., proteins and polysaccharides often assigned to either soluble extracellular polymeric substance (EPS) or soluble microbial products (SMP). Both EPS and SMP are substances produced by microorganisms that are released into the liquid phase as part of the metabolism and due to biological or mechanical stress [61]. Although there is no clear agreement on the exact phenomena occurring on the membrane interface during activated sludge filtration, many publications indicate that EPS play a leading role during fouling formation [61]. More precisely, the non-settleable organic fraction of the activated sludge from the soluble microbial product called soluble EPS or biomass supernatant is often to be of great importance [62].

10.5.2 Retention of Smaller Molecules

Another challenge faced by MBR to produce water of high quality for reuse is the stability and low biodegradability of smaller molecules. One of the main sources of these micropollutants is the administrated pharmaceutical compounds which are excreted from the human body via faeces and urine at a percentage which changes with the compounds. In addition to human excretion, these compounds are introduced into municipal wastewater since hospital wastewaters are generally co-treated with domestic wastewaters.

As a result the wastewater is for instance rich in alcohols, aldehydes, and chlorine-containing compounds such as the recalcitrant chlorophenols arising mainly from the large volumes of used disinfectants. They also are rich in absorbable organic compounds which are the most persistent in the environment, tend to accumulate in the food chain and are often toxic to humans and aquatic organisms. The highest concentrations were found for paracetamol and ibuprofen, ofloxacin and erythromycin and AOX [18].

Although these emerging micropollutants exhibit chemical stability and limited biodegradability, MBR containing a more diverse community of microorganisms with broader physiological capabilities enhance a more complete mineralization, i.e., 30–50% higher than conventional activated sludge system (CAS). MBR also eliminated compounds like mefenamic acid, indomethacin, diclofenac, and gemfibrozil which were recalcitrant for CAS [63]. The role of sludge retention time (SRT) in removal efficiency of several calcitrants have been investigated and confirmed that removal efficiencies were enhanced for several investigated contaminants at longer SRTs. The MBRs in general seem to have longer SRT than CAS. This is considered as one of the main reasons for the better performance by MBR on those contaminants.

Nevertheless, some compounds such as ibuprofen, methyl paraben, galaxolide, triclosan, caffeine were resistant for biodegradation even in MBR [38].

10.6 Future Perspective

As indicated membrane technology in particular MBR system can be utilized to combat the problem of water scarcity and sustainability through water reuse and wastewater reclamation schemes. In particular, use of algal-based or microbial-based MBR holds a great future to reclaim municipal wastewater in an energy-efficient manner while benefiting from a simultaneous production of biodiesel. This eventually may lead to an MBR led zero-liquid-discharge wastewater treatment.

Both membrane biofouling due to EPS and leaking of low molecular weight none-biodegradable contaminants are the two great challenges. As a future perspective considering secondary biological treatments could be effective. A key strategy in this aspect could be the use of an enzyme membrane reactor accompanied with the necessary enzymes. For the emerging contaminants one can focus on the use of oxidizing enzyme such as peroxidase. For the EPS enzymes capable of sensing quorum signal molecules such as acylase and enzymes that can degrade proteins like proteinase should be utilized. In addition, integration of the MBR system with membrane process like forward osmosis (FO), membrane distillation could provide with the required highly purified water [29]. For instance a study on the removal of hormones from wastewater to produce potable water indicated that direct contact membrane distillation (DCMD) provided greater than 99.5% hormone rejection while FO gave 77–99% hormone rejection depending on the experimental condition and the water chemistry [64].

Therefore, MBR combined with emerging membrane processes such as FO and MD, which have demonstrated stable flux, easy membrane cleaning with low energy requirement, can be used to commence the problem of water scarcity. In particular, since many of the arid areas, prone to water scarcity and sustainability are endowed with surplus of solar energy, FO-MBR and MD-MBR accompanied with solar energy could set a sustainable key to resolving the issues of water scarcity through wastewater reclamation and recycling.

On the other hand, certain microbes on continuous exposure to xenobiotics develop the ability to degrade it as a result of mutations. Mutations resulted in modification of gene of microbes so that the active site of enzymes is modified to show increased affinity to a certain recalcitrant contaminant. Certain mutations also resulted in developing new enzymatic pathway for a specific recalcitrant degradation. However, this is after a repeated exposure by a microbe group. And it requires the isolation and culturing of such a group which is often problematic in practice. Therefore, the use of mixed communities of microbes is usually suggested as it has been seen to yield faster results as the different microbes attack different parts through different mechanisms resulting in effective break down. It also creates a condition of co-metabolism. Hence integrating this microbial/algal degradation with membrane process could give better results in terms of water/wastewater recycling.

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Chapter 11
Valuable Products Recovery from Wastewater in Agrofood by Membrane Processes

Silvia Álvarez-Blanco, José-Antonio Mendoza-Roca, María-José Corbatón-Báguena and María-Cinta Vincent-Vela

Abstract Agrofood industry is one of the most important and dynamic industrial sectors worldwide. However, it generates large volumes of wastewaters, which contain great amounts of valuable products. Such products have a wide range of outstanding properties such as antioxidant, anticarcinogenic, or antimicrobial effects. Therefore, significant research has been focused on the development and implementation of different techniques to recover those products from the wastewaters. In the last decades, the utilization of membrane processes has grown in interest since they are considered as 'green processes' and have no negative impact on the valuable properties of these products. This chapter reviews the different membrane separation processes used for the separation, purification, and fractionation of valuable compounds from agrofood wastewaters. Among them, this chapter highlights the recovery of polyphenols and proteins from the fruit and vegetables, dairy and fish and meat industries.

Keywords Agrofood industry · Valuable products · Membrane processes · Proteins · Phenolic compounds

11.1 Introduction

Agrofood industry generates large volumes of wastewaters, which are characterized by high contents of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). In the last years, worldwide legislative regulations have become increasingly restrictive [1]. On the other hand, those wastewaters contain significant amounts of food components (proteins, fat, sugars, fiber, polyphenols, etc.) with remarkable nutritional, biological, and functional properties. Thus, the development

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of methods to recover and reuse valuable compounds from agrofood wastewaters has attracted growing interest. Among these methods, membrane technology offers a number of advantages, such as the operation at mild conditions, favoring the preservation of the properties of food components; the separation of products without the need to add chemicals, with the corresponding economic and environmental benefits; the easy operation and scale up, low maintenance requirements and low costs. However, the main disadvantage of membrane processes is the fouling of the membrane.

Therefore, significant research efforts have been recently dedicated to investigate the potential utilization of membrane technology to recover those valuable compounds. Some of the processes have already been implemented at industrial scale, as it is the case of the production of protein concentrates and isolates from whey, while others are still being tested at laboratory scale. Among those processes special attention is paid in this chapter to the recovery of proteins and polyphenols from different types of agrofood industries wastewaters: dairy industry, fish and meat industries and fruit and vegetables industries. The most often industrially used membrane processes, such as micro-, ultra-, and nanofiltration (NF), reverse osmosis (RO) as well as electrodialysis (ED), and others that are being more recently employed, as osmotic distillation (OD), vacuum membrane distillation (VMD), and direct contact membrane distillation (DCMD), are considered in this chapter. The suitability of all these membrane techniques to remove and recover valuable compounds is reviewed in the following sections.

11.2 Recovery of Valuable Compounds from Whey

The main wastewater obtained in the dairy industry is whey, which is a by-product of cheese and casein manufacturing. It can be defined as the liquid product generated after milk coagulation [2]. Two types of whey can be distinguished depending on the procedure used for milk coagulation. Sweet whey (pH greater than 5.6) is produced by enzymatic coagulation, such as in Cheddar cheese, while acid whey (pH lower than 5.1) is produced as a result of acid-coagulation of the milk, as it occurs in the production of Cottage cheese [3]. Whey represents approximately 85% of the milk volume and contains 55% of milk nutrients. It has a BOD of 35,000 mg O_2/L and a value of COD greater than 60,000 mg O_2/L [4]. Table 11.1 shows the compounds present in whey composition, their properties and potential uses [3, 5–8].

Due to the outstanding nutritional, biological, and functional properties that whey components have and their interest for other industries, such as the pharmaceutical, food or fine chemical ones, whey is often processed using different techniques in order to obtain a wide range of derived products. Some of these treatments are summarized in Fig. 11.1 [8–10].

Among the different products obtained from whey, their protein concentrates and isolates are two of the most relevant at an industrial level. Regarding the former,

Table 11.1 Main components of sweet and acid whey, their properties and potential uses

Component	Composition acid whey	Composition Sweet whey	Properties	Potential uses
Proteins β-lactoglobulin α-lactalbumin Bovine serum albumin Immunoglobulins Lactoferrin Lactoperoxidase Growth factors	0.8%	0.8–0.9%	Emulsifying, encapsulation, gelling and foaming properties Transport activity (retinoid species, iron, etc.) Antioxidant and antimicrobial properties Immunological and anticarcinogenic properties	Health care supplements Infant formulas Food products Functional foods Cosmetics
Lactose	4.3–4.4%	4.9–5.1%	Agglomerating properties Low glycaemic index	Food additive and health care supplements Bakery products Infant formula Pharmaceutical industry
Lactic acid	0.5–0.6%	0.2%	Preservative and acidulant properties	Food additive
Fat	0.1%	0.3%	Creaming properties	Bakery products
Salts Ca, P, Fe, K, Na, Cl, Mg	0.5%	0.4%	Bones and teeth health Protectors against diseases	Health care and dietetic supplements
Vitamins A, D, E, K, thiamine, riboflavin, pantothenic acid, niacin	<10 mg/100 g	<10 mg/100 g	Immunological properties	Health care supplements Cosmetics

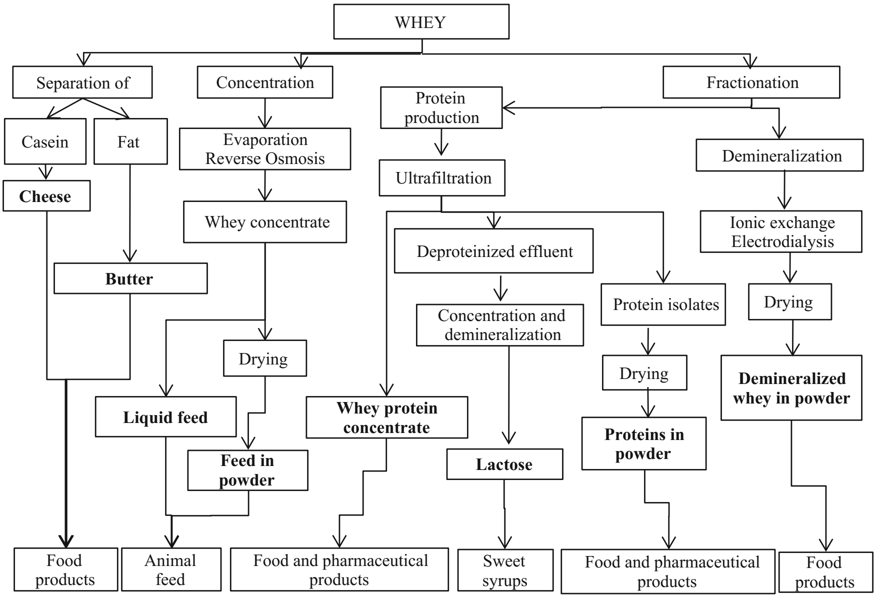

Fig. 11.1 Main products obtained from whey processing

whey protein concentrates (WPC) are usually employed as food ingredients due to their high protein concentration (35–80%); while whey protein isolates (WPI) are used in the preparation of high-added value products, such as pure proteins. WPI has a protein content greater than 85% on a dry basis [11].

11.2.1 Whey Treatment by Membrane Processes

The implementation of membrane separation processes in the dairy industry has increased in the last decades due to several advantages compared to the traditional whey processing methods [12]:

- From the environmental point of view, membrane processes can be considered as "green processes", since they do not require the use of additional compounds to carry out the separation process.
- From an economic point of view, membrane processes are modular and easy to implement in different types of industries.

In addition, the application of the conventional treatments for whey processing (heating) may denature whey proteins, as they maintain their native structures in a limited range of temperatures. This has a negative impact on their functional and biological properties [8, 13].

Among the different membrane separation techniques, the four most often used are those based on a pressure gradient: microfiltration (MF), ultrafiltration (UF), NF and RO.

11.2.1.1 Microfiltration

MF has been used in the dairy industry as a pretreatment mainly to remove fat globules, microorganisms, and bacterial from the wastewaters, due to the open structure that MF membranes possess [12]. Thus, the bacterial quality of whey is preserved. Moreover, fat removal is required if high protein concentration WPC and WPI are produced. Ceramic and spiral-wound membranes are the most often used. Steinhauer et al. [14] studied the influence of temperature on the performance of MF membranes in terms of fouling and protein rejection. They reported that temperatures generally used to avoid microbial growth (lower than 10 °C or higher than 35 °C) favoured β-lactoglobulin adsorption on the membrane surface. In order to clean the MF membranes after they have been fouled with whey, conventional alkaline cleaning agents, such as sodium hydroxide, at temperatures about 50–55 °C are the most widely used [15, 16].

On the other hand, Morin et al. [17] used MF membranes to concentrate the milk fat globule membrane from whey buttermilk. They obtained high purity milk fat globule membrane using a 0.45 μm pore size ceramic membrane (up to a 50% increase from the initial phospholipid content).

11.2.1.2 Ultrafiltration and Diafiltration

Among the membrane separation techniques available nowadays, UF is one of the most widely used to treat whey. Some of those treatments include whey fractionation and/or concentration to produce WPC and concentration of the permeate rich in lactose [18]. To produce WPC, membranes with molecular weight cut-off (MWCO) between 10 and 20 kg/mol are usually considered. At industrial scale, spiral-wound polyethersulfone membranes are the most often used. Several authors performed as well the fractionation of whey proteins by means of UF using charged membranes. For instance, Arunkumar and Etzel [19] fractionated α-lactalbumin from β-lactoglobulin present in milk serum permeate by means of 300 kDa UF membranes with positive charge. The UF process was performed in two stages by recirculating the permeate stream as feed to the next membrane module. These authors demonstrated that dairy proteins with a smaller size than membrane pores can be effectively separated using charged UF membranes. Metsämuuronen and Nyström [20] enriched in α-lactalbumin the permeate stream obtained after UF of diluted whey solutions. Their results shown that hydrophilic membranes were the most suitable to perform the separation in terms of high flux and selectivity. Other applications of UF in whey treatment include the concentration of phospholipids. Konrad et al. [21] obtained a concentrate of milk phospholipids by UF of whey buttermilk using membranes of different MWCOs (30, 50, 100 and 300 kDa). In comparison with MF, these authors achieved higher phospholipid concentration in the retentate.

In diafiltration (DF), UF membranes are employed and feed solutions are diluted by adding water or a buffer. DF can be applied in two basic modes: continuous DF (adding water at the same time as the filtration is performed, without changing solute concentration and feed volume) and discontinuous DF (by diluting feed solution up to a certain volume and then, applying the UF process or viceversa). If protein concentrations greater than 65% w/w in dry basis are desired, DF must be performed.

Membrane fouling is severe in whey treatment by UF and it is mainly due to protein–protein interactions, protein–salts interactions, protein–lipids interactions, calcium phosphate precipitation, and protein–membrane interaction [8, 22]. Different procedures have been proposed to reduce fouling (backflushing, pre-treatment of whey, careful selection of operating conditions, etc.). Moreover, research has been recently focused on improving and developing new membrane cleaning procedures less harmful with membrane structure and using low amounts of chemicals. For instance, the utilization of saline solutions and electric fields has been reported [23, 24].

11.2.1.3 Nanofiltration and Reverse Osmosis

NF and RO are membrane processes that reject divalent and monovalent salts, respectively. NF is mainly used in the dairy industry to reduce salt content while RO is used to concentrate products. The usual demineralization degrees reached by NF are about 35%. Due to the more open structure of NF membranes compared to RO ones, higher permeate fluxes are obtained. Moreover, NF membranes are usually less expensive [8].

Cuartas-Uribe et al. [25] investigated the NF of whey. Authors compared lactose rejection and demineralization degree for two different operating modes: batch and continuous DF. It was demonstrated that both salt removal and lactose enrichment were successfully achieved for a combination of both operating modes. Pan et al. [26] applied NF to demineralise and concentrate acid whey. Obtained results demonstrated that demineralization degree was greater at the pH range that corresponded to the isoelectric point of the main whey proteins (between 4.6 and 5.18). Similarly to that reported by Cuartas-Uribe et al. [25], it was observed that NF in DF mode favored the demineralization rate. Recently, Chandrapala et al. [27] evaluated the performance of NF membranes to separate lactic acid and lactose. Membrane characteristics (MWCO and permeability) had no significant effect on the separation rate, while pH was the main control parameter. This was due to the effect of pH on the degree of dissociation of lactic acid.

Regarding the utilization of RO membranes to treat whey, Madaeni et al. [28] investigated the effect of several operating parameters (temperature of the feed solution, transmembrane pressure, and crossflow velocity) on the permeate flux obtained with a hydrophilic polyamide composite RO membrane. They reported that an increase in transmembrane pressure resulted in an increase in permeate flux up to the limiting value, but it also caused a significant increase in cake resistance, due to the greater compression of the deposited proteins and salt molecules onto the membrane surface. These authors tested as well different cleaning agents to remove those deposits from RO membranes, such as acids (hydrochloride, nitric, phosphoric, and sulphuric acids), alkalis (sodium hydroxide) and surfactants (sodium dodecyl sulfate and cetyle three methyl ammonium bromide). They demonstrated that for most of the cleaning reactants used, there was an optimal concentration beyond which cleaning efficiency decreased. In addition, the higher the temperature of the cleaning solution and the cleaning time were, the higher cleaning efficiency was achieved. For instance, in the case of HCl, the optimal values of concentration and temperature to achieve a flux recovery index of 100% were 0.05% w/w and 35 °C, respectively. On the other hand, González et al. [29] employed an aromatic polyamide spiral-wound RO membrane to concentrate lactic acid that had been obtained from sweet whey UF permeate. Their results demonstrated that the RO process was able to concentrate lactic acid from 32.7 to 100 g/L, achieving a purity greater than 99%. Taking into account these values, a RO plant was scaled up to treat a feed of 10.5 m^3/h, producing 2800 kg per day of lactic acid. The energy consumption was estimated to be 83,472 kWh/year.

11.2.1.4 Electrodialysis and Ion Exchange Membranes

ED is a separation process involving the movement of charged particles towards cationic/anionic membranes by means of an electrical current. This process is especially efficient for whey demineralization, but it is also employed for the fractionation of whey components with similar physico-chemical characteristics (for instance, immunoglobulins and α-lactalbumin) [8]. During the ED process, cationic and anionic membranes are alternatively placed in the ED stack. In this way, anions can permeate through the anionic membranes, while cations permeate through cationic membranes. Thus, demineralised whey is collected in the depletion cell [30]. The maximum reduction in mineral content that can be economically achieved by ED is about 90%.

On the other hand, ion exchange membranes contain ions that are able to exchange with those of the same charge present in whey. As it occurs for the ED process, ion exchange membranes are generally used for demineralization, but they can also be employed for retaining a specific protein (based on its functional, ionisable groups) [8, 30]. Goodall et al. [31] used ion exchange membranes to selectively separate three main whey proteins: α-lactalbumin, bovine serum albumin, and β-lactoglobulin. They obtained a β-lactoglobulin enriched fraction that contained less than 1% of α-lactalbumin and bovine serum albumin using anion exchange membranes.

A number of ED-based processes have been recently developed, such as ED with bipolar membranes (EDBM). In this process, water splitting occurs within a bipolar membrane, which is composed of an anion exchange layer laminated together with a cation exchange layer. Bazinet et al. [32] used EDBM to obtain high purity β-lactoglobulin from WPI. The product contained a 97% w/w β-lactoglobulin.

11.2.1.5 New Value-Added Products from Whey

In the last years, a growing number of research works have been devoted to the recovery of some minor components of whey, such as bioactive peptides and growth factors, by membrane technologies. These peptides have been reported to have a great influence on health. For instance, they have been demonstrated to show positive influence on the control of weight, the immunologic system, bone health, etc. [33] and can be reused in the elaboration of new dairy products. In these works, bioactive peptides and amino acids are fractionated using UF and NF membranes based on their size or charge or they are continuously separated in UF bioreactors [34]. On the other hand, MF and UF have been tested to separate the main growth factors from bovine milk, colostrum, and whey. Gauthier et al. [35] reported that the transforming growth factor β2 was successfully separated from bovine milk and colostrum by a 0.1 μm MF membrane. The growth factor was concentrated up to 70% of the initial content [36]. In addition, Hossner and Yemm [37] reported that UF-DF performed with a membrane of 30 kDa allowed the extraction of insulin-like growth factors I and II from colostrums.

Some of the above-mentioned membrane processes are summarized in Table 11.2, indicating the main operating characteristics of each one.

11.3 Recovery of Valuable Compounds from Fish and Meat Industries Wastewaters

Wastewaters derived from fish and meat industries include all liquid effluents from the processing of the animals, such as washing, cooking, or pressing waters. They contain a great amount of organic matter and other suspended solids. Among them, a significant amount of valuable proteins in low concentrations are present. One of these proteins is gelatine. This fibrous protein has a large variety of industrial applications, from pharmaceutical to food industries, because of its emulsifying, gelling, stabilizing, and foaming properties [38, 39]. Moreover, some fish by-products are treated with enzymatic solutions in order to obtain fish protein hydrolysates. These types of industrial products have grown in interest as a source of peptide fractions with molecular weights between 1 and 4 kDa [40]. The exceptional nutritional and biological properties of such peptidic fractions explain their raising utilization as human and aquaculture food products. They have also

Table 11.2 Summary of several membrane processes to recover valuable compounds from whey

Process	Membrane characteristics	Feed solution and operating conditions	Recovered products	Cleaning procedure	Ref.
UF	PES flat sheet membranes of 30–300 kDa and 0.093 m^2	Whey buttermilk at 10–55 °C, 0.75–2.5 bar and 2 m/s	*Retentate stream*: Phospholipids (purity up to 14%)	P3-Ultrasil 10 (Henkel-Ecolab)	[21]
UF + DF	PES and RC membranes of 30 kDa and 0.1 m^2	Defatted bovine colostrum diluted 1:1 with distilled water at 1.38–1.73 bar and 1.8 L/h	*UF permeate stream*: IGF I and II (recovery up to 8.1 and 3.5%, respectively) *DF permeate stream*: IGF I and II (recovery up to 27.8 and 52.2%, respectively)	ND	[37]
NF	Spiral-wound DS-5 DL (GE-Osmonics) membrane of 150–300 Da and 2.51 m^2	Whey UF permeate at 16–18 °C, 5–25 bar	*Retentate stream*: Lactose (rejection index of about 98% in total recirculation mode)	Water rinsing	[25]
RO	Aromatic polyamide spiral-wound membrane of 0.8 m^2	Whey UF permeate at 25 °C, 30 bar and 2 m/s	*Retentate stream*: Lactic acid (purity higher than 99%)	DIVOS110 and DIVOS2 (Diversey)	[29]
EDBM	Three cationic membranes and one bipolar membrane (total surface area 0.01 m^2)	WPI solutions electroacidified with HC1 at 2 A and 60 V	*Precipitate stream*: β-lactoglobulin (purity of 97%) α-lactalbumin (purity of 2.1%) BSA (purity of 0.7%)	ND	[32]

DF diafiltration; *EDBM* electrodialysis with bipolar membranes; *IGF* Insulin-like growth factors; *NF* nanofiltration; *ND* not determined; *PES* polyethersulfone; *RC* regenerated cellulose; *RO* reverse osmosis; *UF* ultrafiltration; *WPI* whey protein isolates

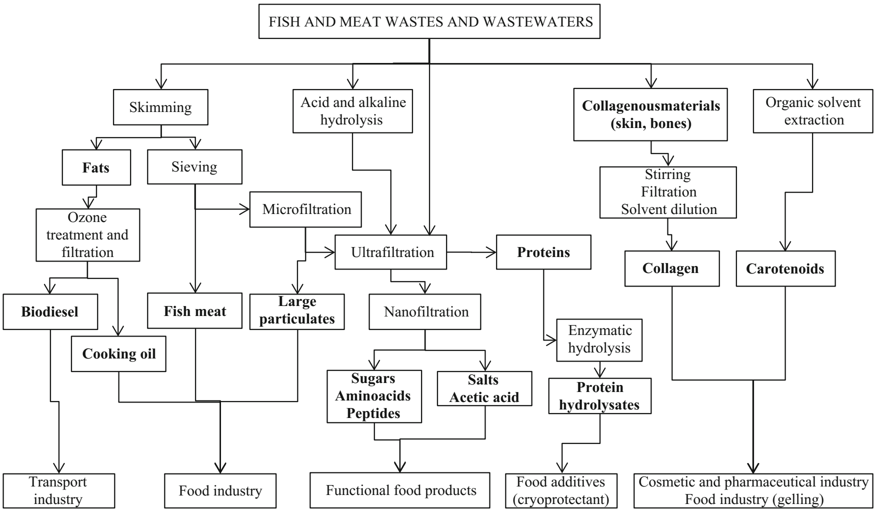

Fig. 11.2 Uses of fish and meat processing wastewaters

been considered for microbial cultures feeding because of their nitrogen content. Figure 11.2 includes some of the most important uses of fish and meat processing wastewaters [39–42].

11.3.1 Wastewater Treatment by Membrane Processes

Membrane separation processes have been used during the last 20 years to extract, concentrate, and purify proteins from fish and meat industries wastewaters and by-products, since classical separation techniques (such as evaporation) are not economically efficient to separate those proteins [43]. In addition, some of the traditional treatments used to recover proteins may change their organoleptic properties. For example, the recovery of blood proteins after decolouration processes may provide salty or bitter taste to those proteins [44].

11.3.1.1 Microfiltration

MF is usually employed as a pretreatment step to eliminate high molecular weight compounds, as well as for reducing fouling in UF, NF, and RO membranes due to the high concentration of suspended matter that fish and meat industries wastewaters contain [45, 46].

11.3.1.2 Ultrafiltration and Diafiltration

As it occurs in the case of whey treatment, UF and DF are widely used membrane processes to recover protein fractions from fish and meat by-products. Afonso et al. [43] compared UF and NF membranes to recover proteins from fish meal wastewaters. A ceramic UF membrane of 15 kDa MWCO was selected and a protein rejection value of 62% when working in concentration mode (volume reduction factor of 2.3) at 4 bar and 4 m/s was obtained. An economic evaluation of the proposed process was also performed and it was demonstrated that UF is an economically suitable technique to recover proteins and diminish the pollutant character of fisheries wastewaters. Economic calculations were carried out taking as a basis a production of fish meal of 170 kg/h. Fixed capital costs were estimated to be 758,910 US$/year and the operating costs (considering a membrane lifespan of 5 years) were 206,237 US$/year, whereof 8.73 and 10.86% corresponded to chemicals and energy consumption, respectively. According to the protein recovery yield of the UF membranes, a yearly revenue of 326,400 US$ was expected. Lo et al. [47] used a 30 kDa polysulfone membrane to recover proteins from poultry processing wastewaters. It was found that almost all proteins were retained by the membrane. More recently, Pérez-Gálvez et al. [48] studied the protein rejection values of three UF membranes with different pore sizes (50 nm, 200 nm and 1.4 μm) when using sardine by-products wastewaters as feed. All the membranes used showed rejections from 77 to 85% of total protein content, as well as reduced the pollutant load of the effluents by about 86%. Due to its pore size, the 50 nm membrane showed the highest protein rejection and COD removal. The membranes were cleaned in a three-step protocol using sodium hydroxide, nitric acid, and sodium hypochlorite at temperatures of 50 °C for the first two stages and 30 °C in the case of the disinfection step.

On the other hand, Simon et al. [38] tested UF and DF processes to concentrate and demineralise fish gelatine liquor from tuna skins using a 10 kDa mineral membrane. They demonstrated that UF provided concentrated gelatine with a narrow molecular mass distribution, which resulted in better gel properties (for instance, viscoelasticity). In addition, DF process allowed the demineralization of fish gelatine without losing a significant amount of proteins during the operating time.

11.3.1.3 Nanofiltration

NF has been proposed to recover low molecular weight peptides and protein hydrolysates. Saidi et al. [40] used NF membranes to concentrate the permeate stream obtained after an UF process of tuna dark muscle protein hydrolysate solutions. Their results demonstrated that the peptidic fraction with a molecular weight lower than 0.3 kDa was concentrated up to 72.5%. In addition, NF membrane fouling index was only about 37% due to the pretreatments performed using UF membranes.

11.3.1.4 Integrated Membrane Processes

Most of the research works proposed hybrid processes that combined several membrane techniques to recover the largest amount of valuable proteins. Bialas et al. [49] proposed an integrated membrane process that included MF, NF, and VMD to recover proteins from the wastewaters obtained in the production of surimi-like material from poultry meat. An overall recovery of proteins of 84% and an average degree of concentration of 9.3 were reported. Moreover, they reached an overall recovery of water of 70% and they indicated that the permeate obtained in the membrane distillation step was appropriate to be reused in the manufacture process. Søtoft et al. [50] considered six membrane steps to recover valuable compounds (proteins, amino acids, salt, acetic acid, and water) from the wastewaters obtained in the production of marinated herring. The membrane steps were: MF (0.2 μm), UF (50, 20, 10, and 1 kDa) and NF. Proteins of different molecular weight are concentrated in the sequential UF steps, while amino acids and low molecular weight peptides are concentrated in the NF step. The authors claim that proteins are concentrated 30 times and amino acids and peptides 11 times compared to the wastewater. The integrated membrane process had a benefit of 39 € per cubic meter of wastewater as a result of sales of proteins and savings in wastewater treatment and fresh water consumption. Other compounds that can be recovered by integrated membrane processes from fish industry wastewaters are aroma compounds. Bourseau et al. [46] reviewed a number of works where membrane technology was used for this purpose and they compared the different alternatives from an economic point of view. Authors selected the work performed by Cros et al. [51], where shrimp cooking juices were treated by a hybrid RO/ED process to simultaneously concentrate shrimp aromas and demineralise the juice obtained in the RO process. A recovery of 80% of total aroma compounds was reported. The best economic-efficient combination was that consisting of an ED membrane area of 60–75% from the total membrane area required (including both RO and ED steps).

The main membrane processes used to recover valuable compounds from fish and meat wastewaters are summarized in Table 11.3.

11.4 Recovery of Polyphenols from Agrofood Industries Wastewaters

Polyphenols are valuable compounds with antioxidant properties that mitigate the effect of reactive species involved in aging and in inflammatory, coronary, and degenerative diseases [52–54]. Therefore, they are of great interest for food, pharmaceutical, and cosmetic industries. They are present in a large number of fruits and vegetables. Thus, they can be found as well in the wastewaters generated during the processing of those products.

Table 11.3 Summary of membrane processes used to recover valuable compounds from fish and meat wastewaters

Process	Membrane characteristics	Feed solution and operating conditions	Recovered products	Cleaning procedure	Ref.
UF	Polysulfone membrane of 30 kDa and 0.003 m^2	Poultry processing wastewater at 0.7–1 bar and 36–48 L/h	*Retentate stream*: Crude proteins (concentration factor of 3.4)	Sodium hypochlorite 200 ppm	[47]
NF	Polyethersulfone membrane of 1 kDa	Tuna protein hydrolysate concentrated by UF	*Permeate stream*: Peptidic fractions with MW lower than 0.3 kDa (concentrated up to 72%) *Retentate stream*: Peptidic fractions with MW of 1–4 kDa (concentrated up to 20%)	ND	[42]
MF + UF + NF	Fluoro polymeric MF membrane of 0.2 µm; polysulfone UF membrane of 50 kDa; Fluoro polymer UF membranes of 1–20 kDa; Polyamide NF membrane	Herring marinade MF conditions: 0.9 bar and 300 L/h; UF conditions: 4.2–7.8 bar and 300–400 L/h; NF conditions: 26.4–29.1 bar and 400 L/h	*MF retentate stream* (5.8% of the initial feed volume) Large particles *UF 50 kDa retentate stream* (3.3% of the initial feed volume) proteins (concentration factor of 30) *NF retentate stream* (9.2% of the initial feed volume)	Sodium hydroxide at pH 9 for MF membranes	[50]

(continued)

Table 11.3 (continued)

Process	Membrane characteristics	Feed solution and operating conditions	Recovered products	Cleaning procedure	Ref.
			Aminoacids and peptides (concentration factor of 11) *NF permeate stream* (41.7% of the initial feed volume) salts and acetic acid		
ED + RO	Cation and anion exchange membranes (total area 0.138 m^2) PES-polyamide RO membrane of 0.033 m^2	Shrimp cooking juices ED conditions: 25 V, 175 L/h and 20 °C; RO conditions: 50 bar and 2.5 m/s	*ED*: Demineralization degree of 91% *RO retentate stream*: Aroma concentrate (recovery of 66%)	HC10.1 M and NaOH 3 g/L for ED and ultrasil 11 5 g/L (Henkel) and hydrochloric acid 2 g/L for RO	[51]

ED electrodialysis; *MW* molecular weight; *NF* nanofiltration; *ND* not determined; *PES* polyethersulfone; *RO* reverse osmosis; *UF* ultrafiltration

11.4.1 Polyphenols from Olives

Olive fruit is a drupe that is characterized by low sugar content and high oil concentration (unlike other drupes) and by a bitter taste caused by oleuropein [55]. Due to the high polyphenols content of olives (2–2.5% of the pulp) [56], effluents from both olive oil production (olive mill wastewater) and table olive processing (in particular fermentation brines or global wastewater from table olive processing and packing) may be sources for concentrates with high antioxidant capacity. Olive oil, essential in the Mediterranean diet, is rich in oleuropein and its metabolites as hydroxityrosol. These polyphenols are potential antitumoral compounds [57]. Many positive health effects of olive polyphenols have been reported in the bibliography [52, 53, 58].

Polyphenols concentration is very variable both in olive mill wastewaters (OMWW) and in table olive processing wastewaters (TOPWW). Furthermore, the types of phenolic compounds also vary in these effluents, depending on different factors such as year of harvest, region, variety, etc. It means that it is very difficult to predict which polyphenols are present in the effluents. For this reason, most of the authors dealing with the management of these wastewaters do not measure individual phenolic compounds but global parameters that take them all into account, such as total phenols and antioxidant capacity.

Total phenols are measured spectrophotometrically according to the Folin–Ciocalteu method. Results are expressed either in mg/L of gallic acid or in mg/L of tyrosol. It is important to highlight that some authors carry out the Folin–Ciocalteu method with raw samples and others with samples previously subjected to extraction [59].

Antioxidant capacity is measured by the total antioxidant activity (TAA). This analysis is normally performed according to the 2,2′-azinobis(3-ethylbenzothiazoline 6-sulfonic acid) (ABTS) method with some modifications [60]. The results are expressed in mmol of Trolox equivalents.

Concerning individual phenolic compounds, their concentration is usually measured by high-performance liquid chromatography (HPLC). In TOPWW, tyrosol, and hydroxytyrosol are the predominant polyphenols. Thus, Ferrer-Polonio et al. [61] only detected these polyphenols in fermentation brines from table olive processing, what coincided with the results reported by García-García et al. [62] for the effluent of a table olive packaging industry. Oleuropein molecule is broken in the debittering process, generating hydroxytyrosol and oleoside-1-methyl ester. This last compound is not stable and its concentration decreases rapidly [58]. Tyrosol is also formed in the debittering process.

In OMWW, catechol, tyrosol, and hydroxytyrosol have been the most identified polyphenols, although protocatechuic acid, vanillic acid, *p*-coumaric acid, caffeic acid, 4-hydroxy-3,5-dimethoxybenzoic acid, 4-hydroxybenzoic acid, 3,4-dihydroxyphenylacetic acid, 2-(4-hydroxy-3-methoxy) phenylethanol, 2-(3,4-dihydroxy)phenyl-1,2-ethandiol and other compounds in lower concentrations have also been reported [63].

11.4.1.1 Recovery of Polyphenols from Olive Mill Wastewaters

Approximately 30 million of m^3 of OMWW are generated in the Mediterranean area. This wastewater is very difficult to treat and high COD values (80–300 g/L) are combined with compounds difficult to biodegrade as tannins, polyphenols, and lipids [64]. The characteristics of the OMWW depend on the method used for oil extraction and type and maturity of the olive, as Paraskeva and Diamadopoulos, [65] reported. Authors summarized the treatment alternatives for OMWW, including membranes in combination with other processes such as advanced oxidation and physico-chemical treatment. Nevertheless, these treatments degrade phenols avoiding the recovery of these valuable compounds.

With the aim of recovering phenols, separation processes that do not cause chemical changes in these compounds are needed. Therefore, combination of conventional filtration with membrane processes can play an important role.

Turano et al. [66] proposed the combination of centrifugation and UF for the management of OMWW. With this process, 90% of COD was eliminated and a permeate rich in salts, sugar, and polyphenols was obtained. However, the separation by centrifugation consumes a lot of energy and separation efficiencies often depend on the addition of a polyelectrolyte. Thus, a combined process only consisting of membrane processes may be more feasible for polyphenols separation.

In the last 10 years, polyphenols recovery has been performed at laboratory scale by means of membrane technologies exclusively. Although the proposed processes have not been implemented at industrial scale yet, there are several patents that have been recently published on this matter. Russo [67] was the first author in proposing a fractionation of the OMWW (this author named this effluent “vegetation wastewater” instead of OMWW) using MF, UF, and RO with the aim of recovering hydroxytyrosol. The reject stream of the RO step is concentrated in this polyphenol.

It seems clear from the different research works performed that the combination of conventional filtration, MF, and UF produces free-suspended solids permeates with low polyphenols rejection. Cassano et al. [60] reported concentrations between 364 and 519 mg/L of total phenols (gallic acid equivalents) in the permeate streams using different UF membranes, with antioxidant capacity between 3 and 8 mMol of trolox equivalents. Authors reported the presence of hydroxytyrosol, protocatechuic acid, tyrosol, caffeic acid, and *p*-cumaric acid.

Other possibility for fractionating OMWW consists of combining UF with NF instead of RO. Thus, the combination of two UF steps and a final NF step with the aim of obtaining a concentrated stream rich in polyphenols was reported by Cassano et al. [68]. Authors proposed as well the valorization of the different streams obtained. Thus, the retentates from the two UF processes could be used for methane production in anaerobic digestion, as they are rich in high molecular weight organic compounds. Moreover, the NF permeate could be reused in the olive oil production process, and the polyphenols contained in the NF retentate can be used for food, cosmetic, or pharmaceutical applications. Recovered polyphenols were mainly hydroxytyrosol, protocatechuic acid, tyrosol, caffeic acid, *p*-cumaric acid, and catechol.

Bazzarelli et al. [69] also described an integrated membrane process for polyphenols recovery from OMWW. It consisted of a MF step for suspended solids removal followed by NF for polyphenols separation, OD for dewatering of the NF retentate and, finally, membrane emulsification for the encapsulation of the phenols in a water-in-oil emulsion. These authors reported that 1463 g of polyphenols could be recovered from 1 m^3 of OMWW.

In addition to pressure-driven membrane processes, other membrane processes have been tested for polyphenols concentration. Thus, forward osmosis (FO) has also been included among the membrane technologies that can play an important role on polyphenols recovery in the future. This process was proposed as a first membrane step for concentrating OMWW previously to UF or NF. A solution of $MgCl_2$ was used as draw solution.

OD could also be used for polyphenols concentration from OMWW. In OD separation is performed by the difference of vapor pressure of water between both sides of the membrane. This is an isothermal process and belongs to the so called “membrane contactors” within the membrane processes. A saline strip solution with low water pressure is used for receiving the water molecules from the OMWW permeating through the membrane due to their higher vapor pressure.

VMD and DCMD are other membrane processes that use the difference of vapor pressure of water between both sides of the membrane to perform the separation. In the VMD, vacuum is produced in the permeate side flowing the volatile components through the membrane and in DCMD the feed is heated; therefore this is a thermally driven process. Both processes have been investigated to concentrate the polyphenols enriched streams obtained by means of other membrane processes. Thus, García-Castelló et al. [70] tested VMD and OD using as feed the permeate of the NF step obtained in the OMWW treatment. OD was selected by its lower energy consumption and a solution with 500 mg/L of polyphenols (56% of hydroxytyrosol) was obtained.

OD and DCMD of OMWW were also investigated by El-Abbassi et al. [59], who applied these processes to raw OMWW and studied both process comparatively. Authors also studied the osmotic membrane distillation (OMD), which combines the driving forces of OD and DCMD. Polyphenols rejection coefficients were very high (close to 99%).

However, the severe membrane fouling indicates that further research has to be carried out before their implementation at industrial scale.

Table 11.4 summarizes the processes proposed by the above-mentioned bibliographical references. Information about membrane fouling shows that the critical membrane step is the first one (MF or UF). Details about the chemicals used in the cleaning of the membranes are also shown.

Table 11.4 Summary of the membrane processes proposed in the literature to recover phenolic compounds from olive mill wastewaters

Process	Valuable stream	Composition of the valuable stream	Fouling/cleaning	Ref.
Centrifugation +UF	UF permeate	Polyphenols (0.2–0.3 g/L); sugars (2–12 g/L); mineral salts (3–8 g/L)	Cake layer formation. Oil concentration enhances the agglomeration of macromolecules	[66]
MF + UF + RO	Retentate from RO	Low MW polyphenols (465 mg/L); HTY (390 mg/L); TY (27 mg/L); oleuropein (15 mg/L); caffeic acid (14 mg/L); protocatehcuic acid (14 mg/L)	Most severe fouling in MF membranes. UF membranes cleaned with NaOH solutions. Very low fouling in RO membranes, flux recovery by water rinsing	[67]
MF + NF + OD	NF permeate after OD	Low MW polyphenols (493 mg/L); HTY (276 mg/L); TY (53 mg/L); oleuropein (65 mg/L); caffeic acid (49 mg/L); protocatehcuic acid (29 mg/L); *p*-cumaric acid (20 mg/L)	Most severe fouling in MF membranes. Cleaning of MF and NF membranes with NaOH solutions (20 and 1 g/L, respectively). Permeability not completely recovered for MF membranes	[70]
OD and DCMD applied to raw OMWW	Stream concentrated by OD and DCMD	Total phenols (up to 9.7 g/L)	Polarization concentration phenomena	[59]
UF +NF	Retentate from NF	Total phenols (86 mg/L); HTY (4 mg/L); TY (40 mg/L); catechol (7 mg/L); caffeic acid (4 mg/L); protocatehcuic acid (30 mg/L); *p*-Cumaric acid (1 mg/L)	Residual fouling after cleaning with enzymatic solutions and KOH in UF membranes. Permeability of NF membranes totally recovered after cleaning with NaOH solution	[68]
MF +NF +OD	NF retentate after OD	HTY (407 mg/L); TY (1785 mg/L); catechol (363 mg/L); caffeic acid (49 mg/L); vanillic acid (7 mg/L)	Permeability of MF and NF membranes totally recovered after cleaning with Ultrasil 50 and 0.1% of NaOH solution	[69]

MF microfiltration; *UF* ultrafiltration; *NF* nanofiltration; *RO* reverse osmosis; *OD* osmotic distillation; *DCMD* direct contact membrane distillation; *OMWW* olive mill wastewater; *MW* molecular weight; *HTY* hydroxytyrosol; *TY* tyrosol

11.4.1.2 Recovery of Polyphenols from Table Olive Processing Wastewaters

Unlike OMWW, TOPWW are characterized by very high salinity due to the preparation process of table olives. Although there are different ways of producing table olives, the process mainly consists of a debittering step with sodium hydroxide and a fermentation process in brine (4–8% w/v of sodium chloride). In the debittering process, oleuropein is hydrolyzed. This is the reason why this phenolic compound is not found in TOPWW. Between 3.9 and 7.5 m^3 of fermentation brine is produced per ton of processed olives [71].

Ferrer-Polonio et al. [61] reported the characterization results of 22 TOPWW samples. Mean values showed pH values around 4, conductivity of 88 mS/cm, COD around 18 g/L and total phenols concentration slightly higher than 1 g/L of tyrosol.

As mentioned above, some authors coincided reporting that only hydroxytyrosol and tyrosol are the polyphenols found in TOPWW, meanwhile a greater number of polyphenols have been found in OMWW. Therefore, separation and further purification of hydroxytyrosol (the most valuable compound) could be more successful from TOPWW than from OMWW. Nevertheless, the enormous conductivity discards RO and other processes as OD for hydroxytyrosol separation.

The membrane process selected for hydroxytyrosol recovery from TOPWW must include UF and NF in order to obtain a stream with enough concentration of hydroxytyrosol for a further concentration. UF seems to be necessary to eliminate completely the suspended solids and oil and greases from the TOPWW. This is a key step, because severe fouling could make the process unfeasible. Thus, the development of new low fouling membranes for this application could be of paramount importance. García-Ivars et al. [72] used photomodified UF membranes in order to obtain low fouling membranes for this application. The membranes showed as well very low rejection index with respect to the polyphenols present in TOPWW.

In the further NF step, hydroxytyrosol can be recovered both in the permeate or in the retentate stream depending on the NF membrane used. Anyway, a further separation of the polyphenols from the brine is necessary, which could be performed by adsorption with resins as reported by Ferrer-Polonio et al. [73].

11.4.2 Polyphenols from Other Agrofood Industries Wastewaters

Membrane processes have also been applied to the recovery of polyphenols from other agrofood industries wastewaters. UF and NF are the most used techniques.

Giacobbo et al. [74] studied the use of NF in the recovery of low molecular weight polysaccharides and polyphenols from effluents from wine production.

Particularly, the effluent from the second racking is rich in these substances. NF divided the effluent into a highly concentrated on polysaccharides reject stream and a permeate stream with polyphenols that can be considered as source of bioactive compounds. Another proposed way of obtaining polyphenols from wine lees from the second racking consisted of a combination of aqueous extraction (for polysaccharides separation) and MF [75].

Conidi et al. [76, 77] evaluated the recovery of polyphenols from wastewaters from artichoke processing (blanching step) by a combination of UF and NF. The total antioxidant activity in the retentate stream from the NF was 43 mMol Trolox.

11.5 Conclusions

Membrane separation processes have been reported to be efficient techniques to recover and valorise high-added value compounds from agrofood wastewaters. For instance, the utilization of membrane technologies to separate, concentrate, and purify proteins from dairy and fish and meat industries as well as phenolic compounds from fruit and vegetable industries have been reviewed in this chapter. Among other advantages, those techniques are increasingly being implemented at an industrial scale due to their low energy consumption and because they do not cause significant changes on the organoleptic properties of the valuable compounds. However, membrane fouling is still a major drawback that limits the worldwide implementation of some of the membrane separation processes described in this chapter at an industrial scale. Research efforts are being made to determine the optimal operating conditions that minimize membrane fouling and to develop new cleaning procedures based on the utilization of alternative physical techniques (such as ultrasounds or electric fields) and less harmful chemical cleaning agents (such as saline solutions).

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Chapter 12
Membrane Operations for the Recovery of Valuable Metals from Industrial Wastewater

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Abstract The development of separation technologies, which also permit the recovery of valuable compounds from industrial wastewaters, reports economic and environmental benefits. In particular, the selective recovery of metals from end-of-life products is an essential strategy to avoid the depletion of natural sources, especially for less abundant metals such as rare earths (REs) and platinum-group metals (PGMs). Although several technologies have been applied in the recovery of metals from wastes, solvent extraction reported the best performance in terms of selectivity when complex matrixes are treated. Regarding solvent extraction, the use of membrane contactors raises against the conventional contactors due to their diverse advantages such as the high interfacial area/volume ratio, the prevention of emulsion formation, the modular design that simplifies the process scale-up and the lower operation cost. This work evaluates the benefits of membrane-based solvent extraction technologies to recover metallic compounds from waste materials through three different cases of study: (i) zinc recovery from spent pickling solutions, (ii) PGMs recovery from depleted car catalytic converters and (iii) rare earths recovery from waste electrical and electronic devices.

Keywords Metals recovery · Rare earths · Platinum-group metals · Zinc · Selective recovery · Solvent extraction

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12.1 Metals as Raw Materials: Production, Price and Usage

Metals are essential elements with specific properties such as elevated boiling and melting points, good electrical and thermal conductivities, high strength and hardness and good malleability and ductility. They can also present magnetic and paramagnetic properties [1, 2].

The aforementioned properties lead metals to be useful raw materials for multiple and diverse applications, making them indispensable to daily life and resulting in enormous production levels [2, 3]. Examples of these applications are the structural use in buildings, transport, telecommunications and electronics.

About 91 of the 118 elements in the periodic table are metals; however, they only represent approximately the 24% of the Earth's crust composition [4]. At the same time, metals have different relative abundance as it is depicted in Fig. 12.1. There are metallic elements with high abundance, like aluminium and iron, which represent the 34.4% and 17.7% of the metals, respectively. The problem lies with the little abundant or scarce metals such as rare-earth metals (0.089%) or PGMs (2.18×10^{-6}%) that require a proper management of the deposits and the search of possible secondary sources (i.e. industrial wastes) that allow their recovery thus reducing their intensive consumption from primary sources.

Apart from the natural abundance of metals, other important indicators, which justify the search of novel metal sources, are their price and production rates as reported in Table 12.1. It should be noted that metals consumed more intensively are those that possess lower prices. Despite the high prices that certain metals can reach in the market, i.e. rare earths (REs) (635 thousand US$/t for the terbium) and PGMs (35 million US$/t for the platinum), their consumption, although at a low rate, is still necessary because of their special characteristics that make them unique for several specific applications of high added value. From this analysis, metals can be classified in two different groups: (i) base metals used in consolidated applications that have low and near constant prices due to their high natural abundance and

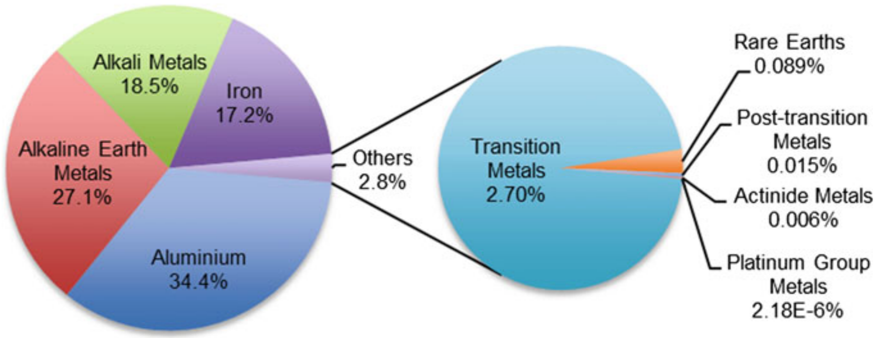

Fig. 12.1 Abundance of metals in the Earth's crust [4]

Table 12.1 Metals price and production volume

Metal	Price (US$/t)	Production (t)
Group 1: base metals		
Iron	46.27 [7]	2000 (Mt) [7]
Aluminium	1460.25 [8]	47,593,000 [7]
Copper	5225.75 [8]	13,415,000 [7]
Lithium	6757.00 [9]	547,000 [7]
Nickel	10,470.00 [8]	3,663,000 [10]
Zinc	1724.25 [8]	13,529,000 [7]
Group 2: minor metals		
Platinum-group metals		
Iridium	17,631,790.93 [6]	3 [11]
Palladium	23,234,701.53 [6]	190 [12]
Platinum	35,307,306.87 [6]	161 [12]
Rhodium	32,290,280.81 [6]	25 [11]
Ruthenium	1,564,776.84 [6]	12 [11]
Rare earths		
Cerium	7253.50 [8]	24,000 [11]
Dysprosium	342,300.00 [8]	–
Europium	421,342.00 [8]	270 [11]
Gadolinium	18,239.10 [8]	7500 [11]
Lanthanum	6683.00 [8]	12,500 [11]
Neodymium	62,755.00 [8]	–
Praseodymium	109,210.00 [8]	2,500 [11]
Samarium	2738.36 [8]	700 [11]
Terbium	635,700.00 [8]	–
Yttrium	43,195.00 [8]	600 [11]

(ii) minor metals subjected to rising prices due to the continuous increase in the demand and their low natural abundance.

Examples of metals in the first group are iron used in steel production and construction, aluminium used in the manufacture of means of transport, nickel used in the manufacture of stainless steel and other alloys, copper used in electrical and electronic equipment, and zinc used in galvanization operations. The most relevant categories of metals in the second group are REs or PGMs that are acquiring importance due to their increment in consumption related to their new and specific applications depicted in Figs. 12.2 and 12.3. The current consumption of REs is focused on the production of magnets for electronic devices such as hard disks, speakers, smartphones, etc. which accounts for 38% of the total consumption [5]. On the other hand, the policies regarding emissions in Europe have led to the requirement of improved catalytic converters in vehicles to reduce gas emissions; therefore, 39, 67 and 69% of the total produced platinum, palladium and rhodium, respectively, are employed in this application [6].

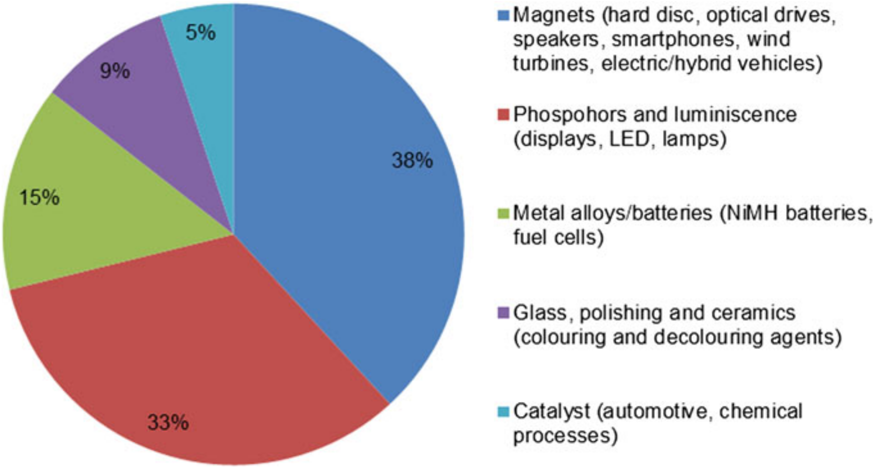

Fig. 12.2 REs usage by application (%) [5]

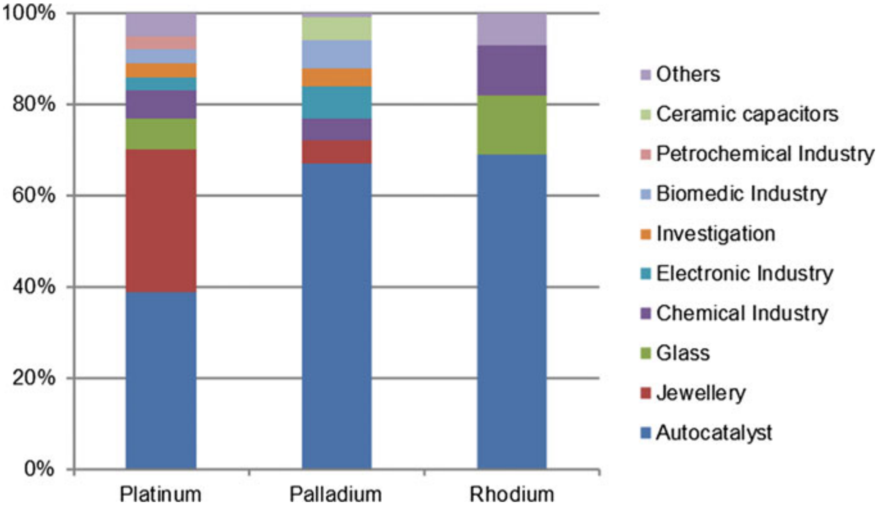

Fig. 12.3 PGMs usage by application (%) [6]

12.2 Conventional and Emerging Technologies for Metal Recovery

This section analyzes potential alternative sources of metals and the main available technologies usually employed to allow their selective recovery. In particular, Table 12.2 compiles different industrial wastes that have been reported in the literature as secondary sources of common metals.

Table 12.2 Secondary sources of common metals

Metal	Waste	Concentration	Volume	Type of waste
Aluminium	Aluminium anodising industry wastewater [13]	15–20 g/L	100,000 t/year EU	Liquid
	Acid mine drainage [14, 15]	293 mg/L		Liquid
Copper	Waste electrical and electronic equipment [16]	2.19 g/L	93.5 million t/year	Solid
	Printed circuit boards [17]	10–30%		Solid
	Acid mine drainage [15]	223 mg/L		Liquid
	Batteries [18]	9.14 g/L		Solid
	Electroplating wastewater [19]	98 mg/L		Liquid
	Fly ash [20]	840–5400 mg/kg		Solid
Lithium	Batteries [21]	5–7 wt%		Solid
Nickel	Acid mine drainage [15]	2.14 mg/L		Liquid
	Batteries [22]	20 wt%		Solid
Zinc	Spent picklig solution [23]	20–120 mol/L	300,000 m^3/year EU	Liquid
	Acid mine drainage [15]	630 mg/L		Liquid

On the other hand, REs and PGMs recycling has significant advantages over mining such as the savings in energy, the lower water and chemicals consumption, and the significant reduction of emissions, effluents and solid waste generation resulting from the extraction and processing of ores [5, 24]. In addition, the concentrations of these metals in secondary sources are often greater than the observed values in ores [5, 25]. However, the main challenges related to the recovery of REs and PGMs from waste streams are [26]: (i) the economic viability of the recovery process due to the typical low metal concentrations and (ii) the presence of competitive species, which might affect the process selectivity. Tables 12.3 and 12.4 present a summary of the state of the art of technologies used in the recovery of REs and PGMs, respectively.

REs are mainly used as raw materials in the manufacture of permanent magnets (38%) [6], which are essential components of electronic devices, speakers, headphones, etc. The scraps generated during the production of magnets have a high content of rare-earth compounds that represent a valuable source for metal recovery. On the other hand, PGMs are mainly used as catalysts. Due to the European emissions policies, automobile catalytic converters based on PGMs have been developed. The increasing demand for new vehicles coupled with the need of replacing exhausted catalytic converters lead to the generation of several millions of tonnes of spent converters every year [28]. Proper management and treatment of spent catalytic converters can turn them into an interesting secondary source of PGMs.

In general, metal recovery can be achieved through pyrometallurgical, hydrometallurgical and biometallurgical methods. Biometallurgical processes are

Table 12.3 Review of secondary sources of REs and their existing recovery technologies [5, 27]

Source	Technology/method	Stage of technology	Existing at industrial scale
Lamp phosphors (Ey, Tb, Yt)	Chemical attack of phosphors and recovery of REEs from the solution by precipitation or solvent extraction	Mature (but still developing)	Yes (Rhodia)
Cathode Ray Tube phosphors (Ey)	Chemical attack and solvent extraction	Limited research (declining interest)	No
Permanent magnets (Nd, Dy, Sm)	Hydrometallurgy	Mature generally but still in lab scale in relation to REE	Investment (Rhodia)
	Pyrometallurgy	Mature generally but not in relation to REE	No
	Gas-phase extraction	Lab scale	No
	Reprocessing of alloys to magnets after hydrogen decrepitation	Lab scale	No
	Biometallurgical method	Lab scale	Planned pilot in 2014
Nickel metal-hydride batteries (La, Ce, Pr and Nd)	Combination of Ultra High Temperature smelting and hydrometallurgy/pyrometallurgy	Mature	Yes (Umicore & Rhodia)
Optical glass (La)	Hydrometallurgy process	Lab scale	No
Glass polishing powder (Ce)	Chemical process	Lab scale	No

based on the use of microorganisms (bacteria, algae or fungi) to carry out metal removal and recovery from aqueous streams. Das [35], reviewed the recovery of different precious metals through biosorption and concluded that biosorption-based processes compared with conventional methods, present advantages such as the low operating costs and the minimization of the volume of chemical and/or biological sludge. Despite these advantages, the development of feasible biosorption technology strategies needs of suitable alternatives for biomass regeneration (desorption) allowing the selective recovery of the target metallic compounds. Dobson and Burgess [41] reached efficacies in the range between 75 and 100% on the removal of heavy metals from wastewater by biosorption. In addition, Zhuang et al. [36], highlighted that waste streams with low metal concentrations are potential niches for biometallurgy, being these methods suitable for the recovery of REs and PGMs.

On the other hand, pyrometallurgical processes make use of thermal energy to promote the separation of metals from solid wastes. In a first step, solid wastes are melted at high temperatures and then different physicochemical processes (i.e. cementation) are applied to allow for the separation of the valuable compounds.

Table 12.4 Review of secondary sources of PGMs and their existing recovery technologies

Source	Reference	Technology	Reference
Spent automotive catalyst (several millions tons/ year [26])	[24, 25, 28–34]	Pyrometallurgy	[25, 26, 29–31, 34–36]
Spent nuclear fuel and high-level liquid waste	[33, 37–39]	Hydrometallurgy	[25, 26, 28–31, 34–36]
Electronic scraps	[26]	Precipitation	[35, 40]
Refining PGMs wastewater	[35, 36, 40, 41]	Solvent extraction	[26, 33, 35]
Industrial wastewater: pharmaceutical, fine chemical, electrochemical and glass sectors	[36]	Ion exchange/adsorption	[26, 33, 35, 40]
Water from geothermal resources (energy production)	[36]	Biometallurgy	[36]
		Biological cyanidation	[25, 29, 30, 34]
		Biosorption	[26, 35, 41]
		Concentration by solar evaporation	[41]

Although these processes have proved to be effective for the recovery of metals from single-component sources [29], they do not provide the required selectivity for multicomponent separations [30].

The lack of selectivity associated to both biometallurgical and pyrometallurgical processes applied to metals recovery from complex matrixes can be improved by the application of hydrometallurgical methods that allow the separation of metals initially contained in aqueous solutions or dissolved after their leaching from solid wastes. Among these techniques precipitation, adsorption [26, 40] or ion exchange [33] have shown great effectiveness in the removal of metals from aqueous streams; however most of the applications reported in the literature are focused on single-component separations.

12.2.1 Metal Recovery by Solvent Extraction

Liquid–liquid extraction is considered as a reference technology to carry out the selective recovery of metals from complex solutions under a wide range of operation conditions namely concentration, pH, volume of solution to be treated, etc. It typically consists in the selective transport of a solute from an aqueous solution to an organic phase either by diffusion or by combination of diffusion and chemical reaction with a selective extractant (facilitated transport) [42]. In a second step, the back-extraction of the solute from the organic phase is carried out using an aqueous stripping solution in order to obtain a concentrated solution from which the metal can be recovered by further treatment (i.e. electrodeposition).

The general requirements of a suitable organic extractant are as follows: (i) low price, (ii) to have a low solubility in water, (iii) to have a good stability in terms of degradability and emulsification, (iv) to be soluble in inert organic diluents (usually aromatic or aliphatic crude oil fractions), (v) to have high loading capacity and good stripping properties, etc. [43].

Ritcey and Ashbrook [44] reported a detailed classification of the commercial extractants usually employed in metal extraction which were grouped according to the extraction mechanism in different categories: (i) carriers based on ion-exchange mechanisms and, (ii) solvating extractants. The first group includes organic acids, which extract cationic species by a cation-exchange mechanism involving hydrogens of the reactive moieties, and chelating carriers, which contain donor groups capable of forming bidentate complexations with metal species. Organic acids usually have reactive groups such as –COOH (carboxylic acids), –P(O)OH (phosphoric, phosphonic andphosphinic acids) and–SO_3H (sulphonic acids). On the other hand, the most common chelating agents are the ketoximes and the salicylaldoximes. The first group is also composed of basic extractants able to remove anionic species. Commercial basic carriers are limited to amines and quaternary ammonium compounds: primary (RNH_2), secondary (R_2NH) and tertiary (R_3N) amines and quaternary ammonium salts (R_4N^+). Finally, solvating extractants are electron-donor compounds that are useful in the removal of neutral inorganic molecules or complexations by adduct formation. These carriers are classified in two categories: compounds containing oxygen bonded to carbon (ethers, esters, alcohols and ketones) and carriers containing oxygen or sulphur bonded to phosphorous. In practice, the most common neutral extractants are the esters of phosphoric, phosphonic and phosphinic acids. For all of them, the oxygen of the phosphoryl group is responsible for the coordination bond formed with the metal. Therefore, more than one coordination bond is possible thus leading to bifunctional complexations.

Recently a new category of carriers namely room temperature ionic liquids (RTIL) is being considered as a promising alternative to design novel extraction processes. RTIL are composed of organic cations and either organic or inorganic anions. They remain liquid over a wide temperature range, including room temperature. The typical cationic groups in RTIL are imidazolium, *N*-alkylpyridinium, tetraalkylammonium and tetraalkylphosphonium ions. The common anions are halides, nitrate, acetate, hexafluorophosphate (PF_6), tetrafluoroborate (BF_4), trifluoromethylsulfonate (OTf) and bis(trifluoromethanesulfonyl) imide (NTf_2). However, most of the applications are based on the use of organic phases formulated with imidazolium-based RTIL [45].

The contact between the phases involved in conventional solvent extraction is usually performed in either mixer settlers or extraction columns. The use of these contactors has numerous disadvantages associated to the coalescence and dispersion phenomena that make necessary additional separation stages that limit the process scale-up [46]. Nevertheless, several industrial applications focused on the application of solvent extraction for metal recovery have been reported [47, 48].

12.2.2 Metal Recovery by Membrane-Based Separation Processes

Membrane-based separation processes offer several advantages over conventional technologies such as the non-dispersive contact between the fluid phases, the high area to volume ratio, the high selectivity, the ease scale-up, etc. As depicted in Fig. 12.4, several membrane-based technologies have been reported in the literature as effective alternatives to recover metals from waste and have been classified in three different groups: (i) filtration processes, (ii) electromembrane technologies, and (iii) liquid membranes [49]. Table 12.5 reports the main advantages and drawbacks of membrane-based separation processes applied to the recovery of heavy metals from wastewater [43].

Filtration technologies refer to those pressure-driven membrane processes able to separate metals by steric (sieving) and solution-diffusion mechanisms [49]. Murthy and Choudhary [50] reported rejection percentages of Nd(III) ions greater than 80% working with synthetic wastewater. On the other hand, electromembrane technologies employ an electric potential as driving force [49]. The electrochemical separation of cerium (product purity > 95%) from mixed rare earths was evaluated by Vasudevan et al. [51] working with current efficiencies of 60%. However, neither filtration processes nor electromembrane technologies provide the required selectivity to carry out the recovery of metallic ions from complex wastewater solutions.

Liquid membrane technologies allow the separation and concentration of a solute using an organic liquid membrane containing a selective extractant that separates the aqueous feed solution and the aqueous receiving phase (stripping

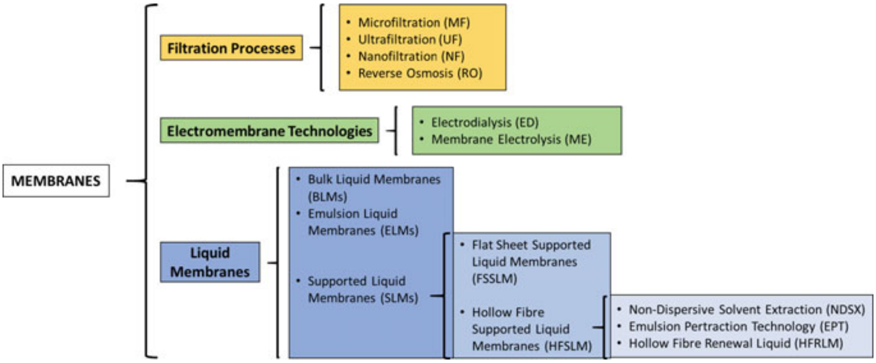

Fig. 12.4 Membrane-based technologies classification [42, 49]

Table 12.5 Main advantages and drawbacks of metal recovery by different membrane-based separation processes (adapted from [43])

Technology	Advantages	Drawbacks
Filtration processes	High separation efficiency Ability to withstand high temperature and wide pH range High chemical and mechanical stability of the membranes	High energy consumption due to high pressure required Prone to membrane fouling High operational costs Membrane requires several backwashing cycles
Electromembranes	High separation selectivity High water recovery	Prone to membrane fouling Requiring periodic maintenance and chemical cleaning
Liquid membranes	Possible usage of inexpensive carriers	Emulsion breakage is the main
	High separation factors	problem associated with ELMs
	Easy scale-up	Poor stability
	Low energy requirements	Difficulty in module design and
	Low capital and operating costs High flux	process configuration Complexities in commercialization

solutions) [49]. Among the different liquid membrane configurations that have been extensively analyzed in the literature, Supported Liquid Membranes (SLM) stand out as suitable alternative to develop processes for metal separation. Table 12.6 compiles several representative applications focused on the treatment of waste effluents containing metallic pollutants.

As depicted in Fig. 12.5, the organic liquid containing an active complexing agent (carrier) is immobilized within a porous structure or solid membrane. The aqueous source and receiving phase are located in two compartments separated by the porous membrane [41].

The development of new membrane-based solvent extraction processes based on the combination of liquid membranes and membrane contactors is a suitable strategy to increase the process competitiveness in terms of process intensification due to the reasons compiled in Table 12.7. Two different membrane shapes are usually employed in the manufacture of membrane contactors: flat sheet and hollow fiber membranes. Plate-frame contactors containing flat membranes have a low area/volume ratio, which makes them useful for fundamental research and unsuitable for developing industrial applications. The most extensive membrane contactors used to perform membrane-based solvent extraction processes are Hollow Fiber Contactors (HFC). HFCs consist of a set of membranes with cylindrical geometry and reduced diameter arranged in a shell and tube configuration. In a typical process, the aqueous phase containing the solute flows through the inner side of the hollow fibers. In the case of hydrophobic fibers, the organic phase (carrier) is pumped through the shell side and fills the membrane pores. To prevent

Table 12.6 Removal of metals from industrial wastes by supported liquid membranes

Feed solution	Liquid membrane composition	Stripping solution	Removal degree	Reference
Fe^{3+} (0.18–18 mol/m^3) sulphate media; pH: acid	$(PJMTH^+)_2(SO_4{}^{2-})$ ionic liquid (1–30% v/v); *n*-decanol (2.5% v/v); n-decane	H_2SO_4 (1000–3000 mol/m^3)	47–83%	[52]
Ni^{2+} (0.17–61 mol/m^3) nitrate media; pH: 2–5	Acorga M5640 (1–20% v/v) + DP8R (1–20% v/v); Exxsol D100	H_2SO_4 (1000 mol/m^3)	–	[53]
Pt^{4+} (625 ppm) and Rh^{3+} (104 ppm)	TOA (tri-octylamine) (8%) in toluene	HNO_3 (8000 mol/m^3)	97% Pt^{4+} and 21% Rh^{3+}	[54]
Cr (3000–7000 mg/L), Zn (11,000–20,500 mg/L) and Fe (15–100 mg/L); pH: acid	Cyanex 272 (10% v/v) in Shellsol D70	H_2SO_4	95% Zn and 98% Fe	[55]
Pd^{2+} (106.4 ppm—1×10^{-3} mol/L) nitrate media; pH: acid	Diglycolthioamides dissolved in kerosene	Thiourea (0.01 mol/L)	>80% mono-TODGTA ≈ 100% di-TODGTA	[37]
Nd (1000–2000 ppm) nitrate media; pH: acid	TODGA, Isopar L and TBP	HCl (0.2 M)	50%	[56]
Zn (80–145 kg/m^3) and Fe (80–90 kg/m^3) hydrochloric media; pH: acid	TBP (20–100% v/v) in Shellsol D70	Service water	79% Zn and 10–30% Fe	[23]

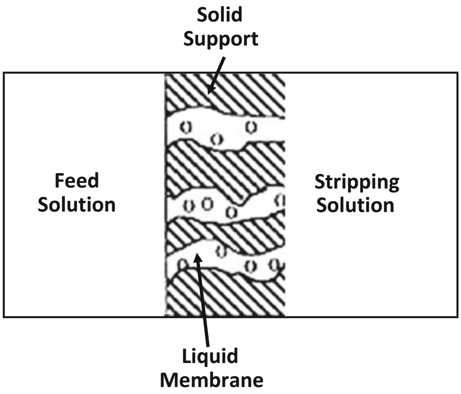

Fig. 12.5 Typical configuration of supported liquid membrane (SLM)

Table 12.7 Advantages and disadvantages of membrane contactors [42]

Advantages	Disadvantages
High interfacial area/volume ratio	Higher fixed costs
Known, constant and independent effective contact area	Membrane introduces an additional resistance to mass transfer
No emulsion formation	Finite lifetime of membranes (replacing costs)
Modular design (simplifies scale-up)	
No different of density between phases is required	
Allows selective separation of target species (use of selective carriers)	
Lower operation costs	

the dispersion of the phases a higher pressure is applied to the non-wetting liquid than to the wetting liquid [42, 46].

The best known commercialized HFC is the Extra–Flow module offered by Liqui-Cel (MEMBRANA). This module uses microporous polypropylene fibers that are woven into a fabric wrapped around a central tube feeder that supplies the shell side fluid. The inner diameter and wall thickness of the fibers are usually 200–220 μm and 30 μm, respectively. The fibers are potted into a solvent-resistant epoxy or polyethylenetube, and the shell casing is polypropylene, PVDF or PVC. The Extra-Flow module contains a central shell side baffle, which improves efficiency by minimizing shell side by-passing. The smallest Liqui-Cel commercial module is 2.62 in. diameter and contains 1.4 m^2 of contact area, while the largest one is 14.0 in. diameter and offers 373 m^2 of contact area [42].

At the same time, membrane-based solvent extraction processes admit different configurations such as non-dispersive solvent extraction (NDSX) and emulsion pertraction technology (EPT) also referred as pseudo-emulsion-based hollow fiber

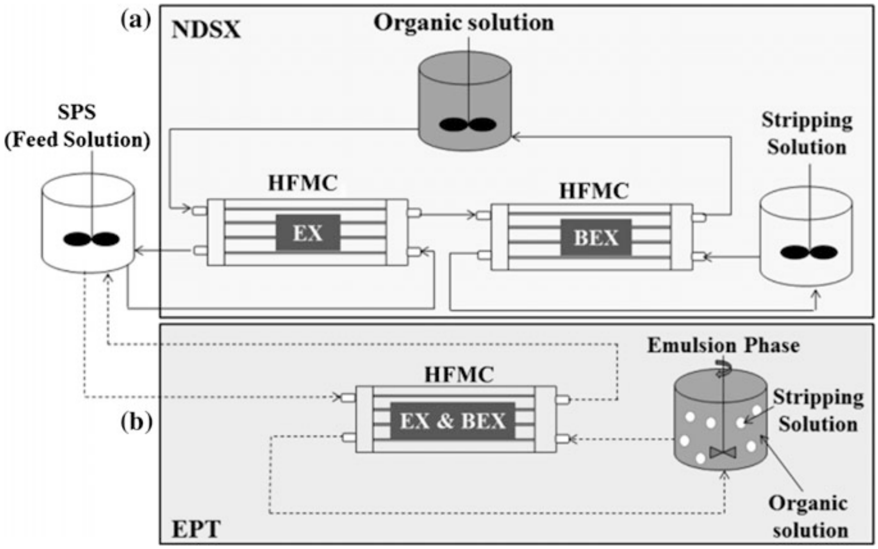

Fig. 12.6 Configurations of the membrane-based solvent extraction processes: **a** NDSX; **b** EPT

strip dispersion (PEHFSD) that differ in the way of contacting the fluid phases and the number of the membrane contactors involved as shown in Fig. 12.6 [23]. In the NDSX configuration (Fig. 12.6a) two hollow fiber modules are employed to carry out the extraction and back-extraction of the target species. In the first module, the aqueous feed phase and the organic phase containing the selective extractant are contacted; in the second module the loaded organic phase is contacted with the stripping solution allowing at the same time, the extractant regeneration and the recovery of the target compounds. On the other hand, in the EPT configuration (Fig. 12.6b) only one contactor is employed to perform the extraction and back-extraction processes. For this purpose, a pseudo-emulsion prepared by dispersing the stripping solution into the organic phase is contacted with the aqueous feed phase allowing the simultaneous removal and recovery of the target compounds. After the mass transfer process, the separation of the organic and stripping solutions is needed.

12.3 Applications of the Membrane-Based Solvent Extraction Technology for the Selective Recovery of Valuable Metals from Wastewater

This section analyzes the application of membrane-based solvent extraction technology using HFC as a feasible alternative to perform the selective recovery of valuable metallic compounds present in industrial wastewater. Three different cases of study have been selected: (i) the recovery of zinc from wastewater produced in the zinc-based surface treatment industry, (ii) PGMs recovery from depleted car catalytic converters and, (iii) REs recovery from waste electrical and electronic equipment.

12.3.1 Zinc Recovery from Wastewater in the Surface Plating Industry

Zinc is a metal with moderate price (US$ 1,724.25/t [8]) and high-volume consumption (13,529,000 t [7]). Traditionally, metallic zinc is produced by combination of hydrometallurgical processes consisting of roasting and lixiviation of ores to produce zinc solutions, which are then subjected to electrolysis. Although this production route allows obtaining zinc of high purity, this process is highly energy-intensive [57].

The electropositive nature of zinc makes it well-suited for use as a coating for protecting iron and steel products from corrosion. For this reason, the surface treatment industry accounts for almost half zinc modern-day demand. The processes involved in the surface treatment of components are predominantly water-based and thus, the generation and management of complex liquid wastes is an issue of concern [49]. Therefore, wastewater produced in the zinc-based surface finishing industry can be considered as a secondary source of both metallic compounds such as zinc and mineral acids. This section illustrates the benefits of combining membrane-based separation steps to achieve the recovery of zinc, as a representative metal in the group of the most abundant metals, from typical waste waters produced in the surface treatment industry. In particular, the management of the spent pickling solutions generated in the hot-dip galvanizing process with high concentrations of Fe^{2+} and Zn^{2+} in HCl media is considered [23, 58–60].

Hot-dip galvanizing consists of covering the surface of iron or steel pieces with a reactive zinc layer that provides oxidation protection. This process is carried out by immersion of the metallic pieces in a bath of molten zinc (450 °C). During the whole process, spent pickling solutions (SPS) coming from stages such as washing, pickling or galvanizing are generated [46]. It is estimated that 300,000 m^3 of SPS are produced annually in the European Union, whose concentrations of zinc, iron and hydrochloric acid are in the range of 20–120, 100–130 and 1.6 mol/L, respectively [23, 58, 59].

SPS are hazardous wastes that should be treated before disposal by an authorized waste management company. These wastes are typically treated by neutralization with lime, thus creating 150,000 t/year of sludge that must be disposed of in landfills. Another method that has been considered appropriate for the treatment of SPS is the Ruthner process, where hydrochloric acid is evaporated and iron oxide granules are formed in a fluidized bed at temperatures around 700 °C. However, the presence of zinc in concentrations higher than 0.5 kg m^{-3} disturbs the process [61].

In order to increase the sustainability and profitability of the surface treatment industry it is needed to deal with the recovery of valuable materials from waste water streams for internal recycling or external reuse allowing at the same time the longest possible service life of process baths and minimizing waste generation [46].

In SPS containing high concentration of hydrochloric acid, different iron and zinc chlorocomplex species are present. Fe^{2+} and Fe^{3+} form only cationic or neutral compounds such as $FeCl^{+}$ and $FeCl_2{}^{+}$, $FeCl_2{}^{+}$ and $FeCl_3$, while Zn^{2+} in the presence of chloride usually forms anionic chlorocomplexes being $ZnCl_4{}^{2-}$ the major species [62]. Therefore, the selective separation and recovery of zinc over iron needs of charge-based separation processes.

Regel-Rosocka [60] reviewed different separation alternatives to regenerate SPS from steel processing aiming at metal recovery. Ion-exchange using solid resins, crystallization and classical and membrane-based solvent extraction were studied. The recovery of zinc from SPS, with reference to the best available techniques (BAT) recommended by EU for the metal processing industry can be carried out using conventional solvent extraction in a cascade of extraction and stripping stirred tanks [63]. Despite this recommendation, the previously discussed disadvantages of conventional solvent extraction, focusing primarily on the phase dispersion, led to consider new alternatives. In this sense, progress in knowledge about membrane processes has allowed to apply membrane-based solvent extraction technologies to the recovery of the metallic zinc contained in acidic SPS, typically containing high concentrations of zinc (80–145 kg m^{-3}), iron (80–90 kg m^{-3}) and hydrochloric acid (219 kg m^{-3}) and other metals like manganese, lead, aluminium, cadmium, nickel, cobalt, etc., that can be considered impurities. Figure 12.7 reports an integrated process to carry out the overall management of SPS allowing the separation and recovery of the main valuable compounds. Initially, membrane-based solvent extraction technology is proposed to separate zinc over iron by the direct treatment of SPS. Two streams are generated: (i) the treated SPS enriched in iron chloride which can be further reused as coagulant after a slight pretreatment and (ii) the stripping solution enriched in zinc and HCl that can be treated by membrane dialysis and electrowinning to recover the acid and the metal, respectively.

Cierpiszewski and co-workers [64] reported tributyl phosphate (TBP) as the most suitable reagent enabling the selective extraction of zinc over iron from HCl solutions, and the subsequent back-extraction with service water. Working with this chemical system under the NDSX process configuration, Ortiz and co-workers [65, 66] reported zinc selectivity values higher than 125 mol zinc/mol iron thus confirming the viability of the separation and recovery process.

Carrera et al. [67, 68] analyzed for the first time, the performance of the EPT process in the treatment of SPS; this work evaluated the influence of the variability in the initial composition of SPS on the rate of zinc chloride separation. The authors concluded that the initial diffusive flux of zinc from the SPS to the organic liquid membrane decreased from 0.1 to 0.03 kg m^{-2} h^{-1} when the initial concentration of zinc in the SPS varied from 80 to 20 kg m^{-3} obtaining average extraction percentages of zinc of 56%.

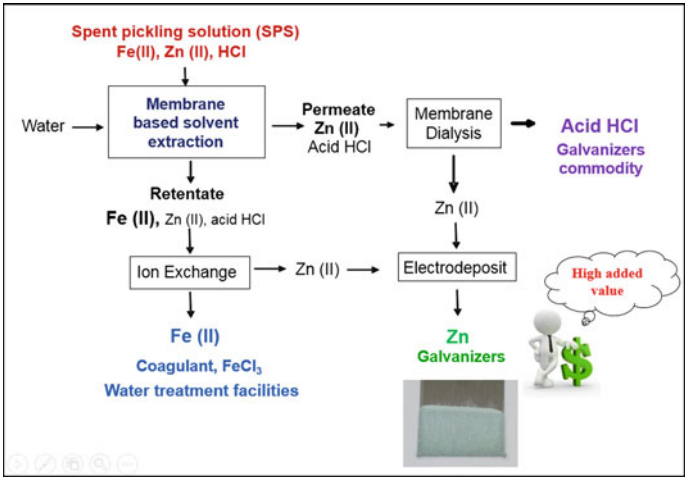

Fig. 12.7 Treatment of spent pickling acids and zinc recovery using membrane-based solvent extraction processes

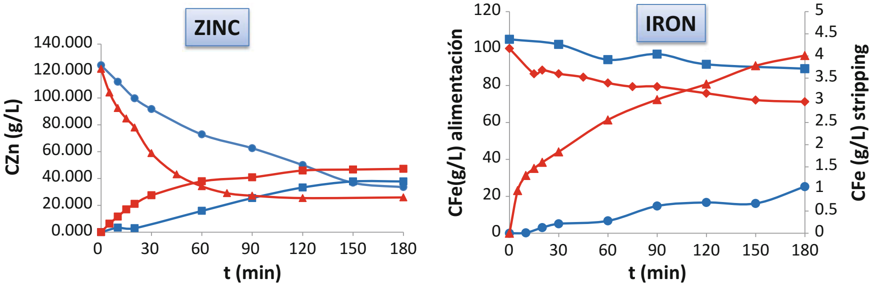

Fig. 12.8 Evolution with time of zinc and iron concentrations in the SPS (*decreasing curves*) and stripping (*increasing curves*) streams working with EPT (*blue curves*) and NDSX (*red curves*) configurations

Laso et al. [23] evaluated the effect of process configuration non-dispersive solvent extraction (NDSX) or emulsion pertraction technology (EPT) on the selectivity of the liquid membrane toward zinc versus iron. The kinetic curves depicted in Fig. 12.8 point out that EPT presents higher extraction and stripping rates due to the higher interfacial area between the dispersed stripping agent and the continuous organic phase in EPT compared to NDSX. However, once reached the equilibrium conditions, about 70% of zinc removal was achieved in both configurations. Nonetheless, iron separation is affected by the process configuration, when EPT is used, the concentration of iron in the spent pickling solutions decreased by 30%, whereas when using NDSX it only decreased by 10%. As a conclusion, NDSX configuration promotes the selectivity of the separation between zinc and iron initially present in SPS.

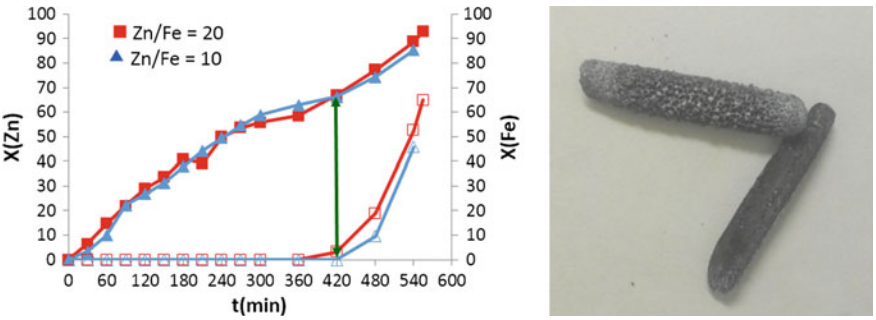

Fig. 12.9 Evolution with time of zinc and iron fractional conversions at −0.7A as a function of the initial Zn/Fe ratio

Carrillo-Abad et al. [69–71] evaluated the electrochemical recovery of zinc from the stripping solutions previously obtained by the treatment of SPS by membrane-based solvent extraction. This process is negatively affected by the presence of iron and chloride, because the oxidation of chloride to chlorine promotes the chemical oxidation of Fe^{2+} to Fe^{3+} which competes with Zn^{2+} ions at the cathode Fig. 12.9 shows the evolution with time of zinc and iron conversion ($X_i = ([M_i]_{\text{initial}}\text{-}[M_i])/[M_i]_{\text{initial}}$) when stripping solutions with different molar ratios Zn/Fe are subjected to electrowinning using an electrochemical reactor with an anionic exchange membrane that separates the oxidation and reduction compartments. It is observed that the reduction of zinc concentration increases up to 70% when no reduction of iron is observed. The process is slightly strengthened at low values of the ratio Zn/Fe. These results allow obtaining a deposit in the cathode containing 99% of zinc as depicted in Fig. 12.9.

12.3.2 PGMs Recovery from Depleted Car Catalytic Converters

PGMs consist of six metals distributed in two groups: (i) the light triad that includes ruthenium (Ru), rhodium (Rh) and palladium (Pd) and, (ii) the heavy triad that contains osmium (Os), iridium (Ir) and platinum (Pt) [72]. Together with gold and silver PGMs are considered noble metals due to their high stability and low chemical reactivity [73].

The main natural deposits of PGMs are found in the Busshvel Igneous Complex (South Africa), the Ni-Cu-PGMs sulphide deposits in Norilsk and Ural Mountains (Russia), the mines in Sudbury (Canada) and Hartley (Republic of Zimbabwe), the Stillwater complex (United States) and the copper deposits of Zechstein (Poland) [74, 75].

On the other hand, the recovery of PGMs from wastes has increased importance in recent years due to their scarcity and high prices. In addition, the isolation of PGMs from secondary sources avoids environmental contamination by decreasing electric consumption [76, 77]. Recovering and refining PGMs from spent materials have already been successfully practiced in many industries, such as Umicore (Belgium), Heraeus (Germany), BASF/Engelhard (USA), Johnson Matthey (UK) and Nippon/Mitsubishi (Japan) [76].

It is clear that new vehicle-emission legislation introduced for example in Europe and parts of Asia in 2014, promoted an increase on the demand for PGMs for developing car catalytic converters. These catalytic converters are based on PGMs, and especially platinum, palladium and rhodium. PGMs are present in automotive catalyst in a quite small concentration [28, 32]: 300–1000 μg/g of Pt, 200–800 μg/g of Pd and 50–100 μg/g of Rh [78]. Despite these small amounts, the concentrations are richer than in mined ores [78], about 2–10 g/tonne [76].

Traditionally, the recovery of PGMs is based on their chemical properties such as their different oxidation states and their capacity to form chlorocomplexes in the presence of chloride anions with different molecular structure and charge depending on the metal concentration and oxidation state and the acid concentration [79, 80]. Platinum and palladium form stable chlorocomplexes namely $PtCl_4^{2-}/PtCl_6^{2-}$ and $PdCl_4^{2-}/PdCl_6^{2-}$, respectively, under a wide range of HCl concentrations. On the other hand, other metals such as Ru, Rh, Os and Ir only form stable species at high concentrations of HCl while aqua-chlorocomplexes are mainly formed at light acidity conditions (i.e. $RhCl_5(H_2O)^{2-}$ and $RhCl_4(H_2O)_2$ for rhodium) [81, 82].

The recovery processes are focused on the direct recovery of platinum and palladium from the raw material being minor metals isolated by further treatment stages. Several works have been published dealing with PGMs recovery from natural ores and spent automotive catalyst using different hydrometallurgical and pyrometallurgical methods [29, 32, 76, 78, 83, 84].

Figure 12.10 shows a typical process for the recovery of PGMs [85]. Raw materials are pretreated to separate primary metals before recovering noble metals. Then, the mineral is contacted with a mixture of nitric acid and hydrochloric acid (aqua regia) in order to facilitate the leaching of gold, platinum and palladium. Other secondary PGMs such as rhodium, osmium, ruthenium and iridium are further recovered from the solid waste generated in the first step. Gold is first precipitated using ferrous sulphate as reducing agent. Platinum is recovered as ammonium hexachloroplatinate, which is subjected to calcination and several stages of redissolution and precipitation to produce the pure metal. Palladium is precipitated as palladium (II) diaminchloride. Its purification is performed similarly to platinum.

While various hydrometallurgical processing routes have been suggested, solvent extraction seems to be the most favoured route for the extraction, purification and separation of PGMs from the complex leach solutions generated during processing. PGMs are also produced by a combination of solvent extraction stages; this alternative improves the selectivity of the separation and consequently, the purity of

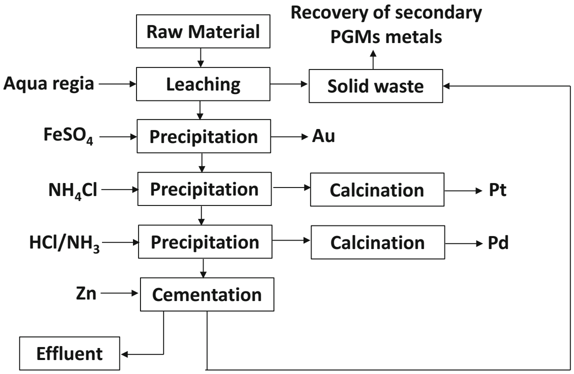

Fig. 12.10 Conventional process for the recovery of PGMs (adapted from [85])

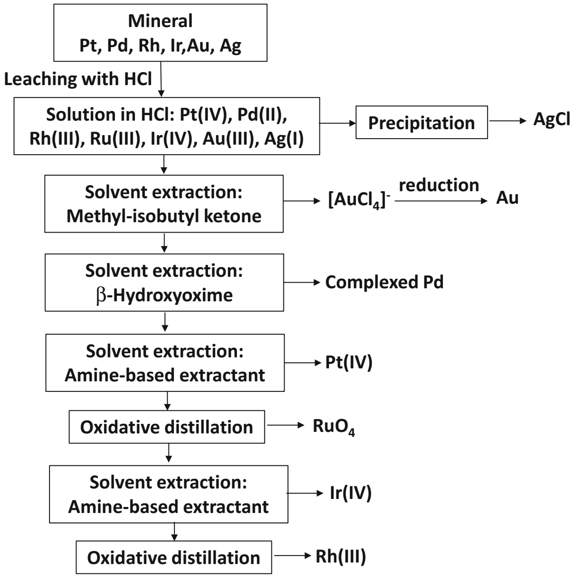

Fig. 12.11 Solvent extraction process for the recovery of PGMs (adapted from [86])

the metals. Figure 12.11 illustrates the solvent extraction process used by Matthey Rustenburg Refiners (South Africa) to perform the selective recovery of PGMs [86].

The typical extraction mechanism for PGMs is based on the formation of a neutral ion pair between the metal chlorocomplex and the protonated carrier. Common extractants employed for the selective separation of PGMs are basic amines or quaternary ammonium salts. The strength of the ion pair depends on the carrier basicity (primary amines $\ll$ secondary amines $\ll$ tertiary amines $\ll$ quaternary ammonium salts) and therefore, the stronger the interaction the better metal extraction and the lower selectivity [87]. In conclusion, the selection of the proper selective carrier strongly depends on the characteristics of the separation problem.

Table 12.8 Selective carriers employed in the recovery of PGMs from HCl media

Organic phase	Feed solution	Reference
Tertiary amine (Alamine 304) in xylene	Pt(IV)	[88]
Tri-octylamine (TOA) in toluene	Pt(IV), Pd(II) and Rh(III) Pt(IV) and Rh(III)	[89] [54]
Quaternary ammomium salt (Aliquat 336) modified with dodecanol in toluene	Pt(IV)	[90]
Amine-based extractants	Pt(IV)	[91]
Tri-iso-octylamine (Alamine 308) in kerosene	Pt(IV) and Rh(III)	[92]
Tri-octyl/decyl amine (Alamine 336) modified with n-decanol in kerosene/Undiluted tributyl phosphate (TBP)	Pt(IV) and Pd(II)	[93]
Tri-n-octylamine (Alamine 300) modified with TBP in kerosene	Pt(IV) and Pd(II)	[94]

Table 12.8 compiles different examples of carriers and solvents employed for the separation of PGMs in chloride media reported in the literature.

While these liquid anion exchangers generally yield high recoveries, often from chloride solutions the amine/hydrochloric acid system is known to favour the formation of third phases and emulsions during the dispersion of the organic and aqueous phases, affecting the mass-balance and hence the recovery yields in an industrial solvent extraction mixer-settler cascade. To overcome this problem, the use of membrane-based solvent extraction has been explored as an alternative to recover PGMs, as reported in Table 12.9.

12.3.3 REs Recovery from Waste Electrical and Electronic Equipment (WEEE)

The demand of RE elements is continually increasing, with a high risk of supply disruption [98]. Currently China has over 90% of the market share, although the country possesses less than half of the global deposits [27, 99].

Production of rare earths is often associated with environmental issues that can be mitigated by metal recovery from postconsumer products [56, 99].

A huge variety of end-of-life products are available for rare earth recovery, nevertheless, the actual rare earth recovery is estimated to be less than 1% due to low efficiencies and limitations of the recycling processes. Therefore, it is imperative to develop and improve an effective rare earth recycling process [56].

Waste electrical and electronic equipment (WEEE) and, in especial, the permanent magnets contained in those equipments are considered an important target for REs recovery [99]. Different technologies have been explored for the recovery of REs from permanent magnets, such as: hydrometallurgy and pyrometallurgy

Table 12.9 Recovery of PGMs by membrane-based solvent extraction

Feed solution	Organic phase	Stripping phase	Contactor characteristics	Recovery	Reference
10 ppm Pt(IV)/Pd(II) NaCl 0.5 M pH = 2	Aliquat 336	NaCl 0.5 M $NaClO_4$ 0.5 M Thiourea 0.5 M Thiocyanate 0.5 M	Dialysis cell with activated composite membranes or hybrid membranes	Recovery of Pt: 30-84% Recovery of Pd: 30%	[95]
Rh(III) 500 mg/L in HCl concentrated pH = 1	Aliquat 336 in dodecane	1 M NaCl	Microporous support: polydifluoroethylene, thickness 125 µm, porosity 75% and pore size 0.2 µm		[96]
Rh, Pd and Pt 500 mg/L in HCl concentrated pH = 1	Aliquat 336 (module II) + Cyanex 471 (module I)	0.1 M NaSCN (module I) + 0.5 M $NaClO_4$ (module I) pH 2	Hollow fiber membrane contactors	Recovery: 75% Pd and 65% Pt	[78]
Pd(II) 0.001 M in HCl media	o-nitrophenyl octyl ether and Cyanex 471X	0.5 M KSCN	Polymer inclusion membrane: cellulose triacetate, 12.56 cm^2	>87%	[97]

processes and gas-phase extraction [27, 56]. Pyrometallurgical processes utilize high temperatures to chemically convert the components of WEEE wastes into valuable REs. They require a large energy input and generate large amounts of solid waste [27, 56, 100]. Gas-phase extraction route is based on volatility differences involving chlorination and carbochlorination, but corrosive aluminium chloride and hydrogen chloride gas generated from this process present serious environmental and safety hazards [27, 56, 101, 102]. Solvent extraction, leaching and precipitation are the most representative hydrometallurgical processes [27, 56]. The conventional process employs strong acids to dissolve REs from end-of-life products, which are then selectively precipitated using basic solutions.

Hydrometallurgical processes are often preferred over other types of processes because they are able to handle lower grade and more complex streams and they result in higher product purity [99]. However, they also present disadvantages such as a high consumption of chemicals and a higher generation of secondary waste streams, which require additional processing [27, 56, 99]. At industrial scale, solvent extraction of REs is achieved using counter current phase contactors, such as mixer settlers and pulse columns [99].

REs form different species depending on the type of mineral acid employed for their leaching from the primary or secondary sources and thus, the selection of the selective carrier depends on the specific characteristics of the feed solution. McGill [103] analyzed different types of extractants useful in the selective extraction of rare earths. Neutral extractants, such as tributyl phosphate (TBP), are the carriers that exhibit greater selectivity, especially in nitrate media. The typical reaction for the extraction of rare earth (RE) in nitrate media is reported below:

$$\mathrm{RE(NO_3)_3}\cdot x\mathrm{H_2O} + 3\mathrm{TBP} \rightarrow \mathrm{RE(NO_3)_3 3TBP} + x\mathrm{H_2O} \tag{12.1}$$

On the other hand, acidic extractants, such as bis-(2-ethylhexyl) phosphoric acid (D2EHPA), are employed to remove cationic species by the following cation-exchange extraction process:

$$\mathrm{RE^{3+}} + 3\mathrm{HL} \rightarrow \mathrm{REL_3} + 3\mathrm{H^+} \tag{12.2}$$

At industrial scale, several extractants were used for the separation of Res [99, 104–106]: bis-(2-ethylhexyl) phosphoric acid (D2EHPA, HDEHP), 2-ethylhexyl-2-ethylhexyl-phosphonic acid (HEHEHP, PC-88A), dialkyl phosphinic acid (Cyanex 272), neodecanoic acid (versatic acid), phosphine oxides (Cyanex 921 and Cyanex 923), tributylphosphate (TBP) and phosphorus-based chelating extractant (Cyanex 572). In summary, acidic extractants are widely used in industrial practice, but they suffer from relatively low REs selectivity due to simultaneous co-extraction of other cations such as Fe, Cu and Ni [107, 108]. On the other hand, neutral extractants such as tetraoctyl diglycol amide (TODGA) and trialkyl phosphine oxides (Cyanex 923) provided the required selectivity to separate REs elements [109–111]. In particular, Kim et al. [56] proved that Cyanex 923 and

Table 12.10 Applications of membrane-based solvent extraction to recover REs

Feed solution	Organic phase	Stripping phase	Contactor characteristics	Recovery	Reference
1000-2000 ppm Nd Nd–Fe-B magnets in 1–6 M HNO_3 and 3–6 HCl	Extractants: TODGA or Cyanex 923, and TBP. Solvent: Isopar L Ratio 3:4:3	0.2 M HNO_3	Hydrophobic hollow fiber modules (polypropylene): area 100 cm^2, ID 0.25 mm, 700 fibers	50% recovery	[56]
Nd(III) 106.7 mg/L in nitrate media pH = 4.5	0.5 M DNPPA	3 M H_2SO_4	Hydrophobic hollow fiber modules (polypropylene): 35,000 fibers, area 14,000 cm^2	98% extraction and 95% stripping	[113]
Nd(III) 100 mg/L in nitrate media pH = 4.5	0.5 M HEHEPA	4 M HNO_3	Hydrophobic hollow fiber modules (polypropylene): 35000 fibers, area 14,000 cm^2	95% extraction and 87% stripping	[114]
Nd(III) in nitrate media	DNPPA or TOPO in petrofin	HNO_3	Hydrophobic hollow fiber modules (polypropylene): 9950 fibers, area 14,000 cm^2	99.9% recovery	[115]

TODGA are highly selective towards rare earths in permanent magnets where other metals such as Fe, B, Cu and Ni are present in the outer coating.

Kim et al. [56] also investigated a membrane-based solvent extraction system for the recovery of REs from commercial NdFeB magnets (procured by Molycorp Magnequench, with a 30% of REs content). It was concluded that only Nd, Pr and Dy were selectively extracted from the scrap magnets into the strip solution without co-extraction of non-rare earths such as Fe and B. These results demonstrate the viability of membrane-based solvent extraction process for the selective recovery of REs from industrial scrap magnets. In addition, membrane-based solvent extraction in the REs recovery from scrap magnets results in a more environmentally friendly and cost-effective process compared to the conventional routes such as precipitation and solvent extraction. Bringas et al. [46] compared conventional and membrane-based solvent extraction technologies using process intensification metrics, the productivity/size ratio (PS) and the modularity (M), previously developed by Criscuoli and Drioli [112]. The calculated value of the index PS was 11.7 confirming the lower size of the membrane equipment required to achieve the same productivity obtained using a cascade of mixer settlers. On the other hand, the value of the modularity index (M) calculated at different levels of productivity was $0.73 < 1$, thus confirming the benefits of employing the membrane-based process versus the conventional technology for scale-up purposes. Table 12.10 summarizes other examples of application of membrane-based solvent extraction technology to recover REs.

12.4 Conclusions

Membrane-based separation processes have been demonstrated as an alternative to carry out the recovery of valuable compounds from wastewaters due to its potential to replace conventional processes by accomplishing selective and efficient transport of specific components. In particular, membrane-based solvent extraction processes based on facilitated transport offer additional advantages due to their ability to promote the selective transport of the target species by the coupling between mass transfer and chemical reaction. However, the application of individual membrane processes often fails to selectively recover the valuable materials present in complex wastes. Therefore, the development of integrated processes consisting of single membrane separation stages is a promising strategy to design eco-innovative processes.

In particular, the supply of metals is increasingly under pressure as demand increases and as they are subject to challenges from price volatility, availability and geopolitical issues. Therefore, their selective recovery from industrial wastes is essential to avoid the depletion of natural sources, especially for less abundant metals that are subjected to a continuous increasing consumption.

As a proof of concept, the initial hypothesis has been illustrated along the text through three different case studies focused on the recovery of heavy metals belonging to two different categories namely based metals and minor metals. In particular, this work evaluates the benefits of membrane-based solvent extraction technologies to recover metallic compounds from waste materials through three different cases of study: (i) zinc recovery from spent pickling solutions, (ii) PGMs recovery from depleted car catalytic converters and, (iii) rare earths recovery from waste electrical and electronic devices.

From the analysis previously undertaken, it is concluded that membrane-based solvent extraction employing HFCs is an efficient alternative to recover cationic or anionic metallic species from complex wastes due to the wide variety of available selective carriers. Although a high number of lab scale applications of this technology dealing with the recovery of valuable metallic species has been reported, the number of industrial applications is still limited. Therefore, the implementation of this technology to develop high-scale applications needs of design methodologies that consider the long-term assessment of the technology and the process scale-up.

The main issues to be considered to carry out the industrial implementation of membrane-based solvent extraction technology are as follows: (i) development of accurate mathematical models able to describe facilitated transport mechanisms and essential for process design and operation, (ii) long-term analysis of the selective extractant stability, (iii) economic evaluation of the process taking into account both fixed and operation costs, (iv) integration of the membrane-based solvent extraction technology in the industrial process and (v) risk and environmental assessment of the technology.

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Chapter 13
The Potential of Membrane Technology for Treatment of Textile Wastewater

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Abstract The textile industry is characterized by being a very demanding consumer of high-quality water. Thus, both quantity and quality of water are key issues that affect this sector considerably. However, in a global context in which water is becoming the twenty-first-century paragon, the choice of wasting water is not anymore acceptable. The textile industry is facing thus a double objective: to minimize drastically the water consumption while using water with high quality. This objective involves that (1) reuse of water is essential, and (2) effective and economic processes to recover the quality of water are required. Membrane technology offers the possibility to do that at low expenses. The potential of membrane technology to treat wastewater and recover both the water itself and the pollutants (organic and inorganic substances), which become then valuable compounds, has been demonstrated in the recent research. Nanofiltration is one of the most attractive technologies for this application since nanofiltration membranes can retain ions and small organic molecules from an aqueous solution. But it is also very challenging due to the presence of salts and operating problems such as fouling, salt deposition, etc. This book chapter summarizes the main achievements of nanofiltration in the textile industry, focusing on three different scenarios: (i) nanofiltration as stand-alone technology; (ii) nanofiltration in hybrid processes, and (iii) nanofiltra-

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tion in water fractionation (recovery of water, dyes and salts). The last advances on nanofiltration as well as the main limitations and challenges still to be faced are also described in order to guide the reader toward further research.

Keywords Textile processing · Wastewater · Pressure driven membrane filtration · Nanofiltration · Ultrafiltration · Concentrate treatment · Advanced oxidation · Hybrid processes · Dyes · Resource recovery · Water recycling

13.1 Introduction

In the textile industry, and in particular the textile finishing sector, the availability of high-quality water is a key factor in many processes such as washing, bleaching, printing, and coating of textile products (yarns, woven fabrics, knitted fabrics, nonwoven fabrics, ready-to-wear articles, etc.). Textile companies often face a reduction of available water sources, not only because of water scarcity but usually as a result of permit systems, which limit the use of ground water to a predetermined volume; the permit may be conditional, related to the company's efforts to find possibilities for water reuse. In the future, many of these companies will face the requirement of reusing a significant part of all incoming fresh water. This involves an improvement of the wastewater quality to the standards used for fresh (ground) water. Traditionally used methods are insufficient for obtaining the required water quality. Current wastewater treatment methods are primarily based on biochemical degradation using, e.g., activated sludge systems. The reason for this is mainly related to the cost of treatment required to meet discharge standards. The use of oxidative microbiological systems may seem logical from the point of attaining these standards, since this approach is feasible and cost-effective for decreasing the concentration of organic pollutants. However, the current objective for wastewater treatment systems has shifted toward water reuse and considers wastewater as a source rather than a waste. In this context, the advantages of conventional systems are reversed; oxidative biochemical conversions may not be attractive anymore since they do not fractionate but degrade organic compounds so that water is left with a residual concentration of organics and nutrients, which is difficult to treat further in a closed system of water usage. At the same time, voluminous secondary waste fractions such as concentrates or sludge are produced. These constitute large-scale unsolved problems. Current wastewater treatment practices are therefore unsustainable. Integration of the water reuse objective into this conventional approach naturally leads to low-quality applications of recycled water, and to an increase in the volumes of secondary waste. Furthermore, the fraction of water that can be reused is limited, with significant losses in waste or side streams.

As a starting point, it is observed that dye baths produce large wastewater streams that cannot be discharged directly because they would have a dramatic impact on the quality of the total wastewater stream. Used dye baths contain high concentrations of organic compounds, combined with a very high concentration of inorganics. Purification and reuse is therefore advisable, in view of the decrease of the wastewater amount as well as the decrease of the water consumption. Membranes can be used for the purification of these complex wastewater streams [1–4]. The membrane process that best meets the requirements is nanofiltration, because nanofiltration membranes can retain ions as well as relatively small organic molecules from an aqueous solution [5]. This stimulated the interest in research on applying nanofiltration for textile wastewater, which is challenging, since most wastewater fractions in the textile (finishing) industry contain high concentrations of organics as well as salts. Although a large diversity can be found in textile finishing baths, a significant fraction of organic compounds is always present; the inorganic fraction may range from absent to 10 wt%. All further considerations concerning treatment methodologies for an integrated water management system will take this range of concentrations into account. For nanofiltration, this gives a risk of several membrane problems: organic fouling, salt deposition, high osmotic pressures, and correspondingly, low fluxes. Thus, the application for textile wastewater is probably one of the most difficult ones for nanofiltration.

Intensification of processes may even go further and consider recycling of various components of textile wastewater. Process intensification requires an innovative approach by optimizing the integration of different sub-processes in a novel concept; membrane technology is expected to play a leading role in this field [6]. This responds to the changing paradigm in wastewater treatment from meeting effluent standards in view of protecting receiving water bodies, ensuring good quality of surface waters and groundwaters, and protect the human population against dissemination of toxic chemicals and infectious diseases, to a new challenge of exploiting wastewater as a useful source of not only water, but also energy, nutrients, and chemicals.

The various treatment levels of textile effluents using nanofiltration or nanofiltration-based methods are described in this book chapter. Three ranges of applications are distinguished. First, straightforward, stand-alone application of nanofiltration for textile effluents is considered. This is applied in view of environmental protection, and of producing recycled water. Second, integrated and hybrid systems are described, in which an overall solution is developed instead of focusing only on the produced permeate water. A third and last approach is in fractionation of water, dyes, and salts, with the eventual aim of zero liquid discharge, or near zero liquid discharge.

13.2 Classical Membrane-Based Solutions for Textile Wastewater

Nanofiltration (NF) technology can be a competitive alternative to conventional processes for treatment of textile wastewater. The advantageous attributes of NF technology, in terms of high solvent permeability, easy up-scaling, and ease of chemical cleaning, suggest that membranes may become the mainstream technology for textile wastewater treatment. The first objective of using nanofiltration was in environmental protection, i.e., reducing pollutant loads in wastewater discharge. Nanofiltration was an interesting option, since classical processes would not yield a very good water quality, and were challenging in operation. However, it became soon clear that the potential of nanofiltration goes much beyond this objective: the process would produce a high-quality permeate water that easily meets standards for reuse. As a consequence, many studies highlighted the use of nanofiltration for recycling textile wastewater. In all these studies, the focus was double: (a) reducing wastewater volumes, and (b) producing water that can be reused. In many cases, this is applied after a biological treatment. In some cases, application at elevated temperature is considered, which gives a third benefit by reducing the need for heating when water baths are reused at higher temperature. Evidently, this can be only practiced by skipping biological treatment. Such direct nanofiltration of dye baths may be a further attraction of nanofiltration [7]. By applying direct nanofiltration, the organic material can be retained more easily because the components are not decomposed in the biological treatment and thus larger, so that rejections are higher. On the other hand, the concentration is higher, and more problems with membrane fouling are expected.

There are no strict guidelines determining the required quality of process water in the textile finishing industry. Generally, setting the targets for process water quality in the textile industry would depend on the strategy of individual companies. In most cases, such targets are related to water turbidity, and the water hardness, which should be in the normal range for relatively soft ground water (not more than 50–60 mg/L). Thus, turbidity of water for reuse should be less than the turbidity of the groundwater that is used for processing. Of course, all remaining color should be removed before reuse. Furthermore, no other components such as heavy metals can be allowed in the water cycle [8].

The quality of the NF permeate is comparable to typical groundwater in hardness ($\sim$40 mg/L Ca or 10 °F), concentration of organic compounds and turbidity. Table 13.1 gives the composition of the permeate obtained with three typical NF membranes, and the composition of the feed water used [9]. The permeate with NF70 was colorless; small fractions of UV-absorbing compounds were left in the permeate obtained with UTC-20 and NTR 7450, which are membranes with larger pores. The permeate quality is strongly dependent of the membrane type; for a total decoloring a membrane with small pores (NF70) is needed to remove the smallest compounds as well, but fluxes may be low due to the osmotic pressure (high

Table 13.1 End-of-pipe treatment of textile wastewater with three NF membranes (NF-70, NTR 7450, UTC-20; pressure 10 bar) [7]

Parameter	Feed	NF-70	NTR 7450	UTC-20
pH	8.3	9.3	8.6	8.6
Suspended solids (mg/l)	18.8	<1	<1	<1
Ca (mg/l)	85.6	0.6	27.8	9.6
Cr (μg/l)	140	<10	10	<10
Fe (μg/l)	360	<10	10	<10
Zn (μg/l)	610	13	149	17
COD (mg O_2/l)	231.8	17.7	31.4	33.4
BOD (mg O_2/l)	5.2	<1	<1	–
Conductivity (mS/cm)	3.8	0.11	2.29	1.78
SO_4^{2-} (mg/l)	313	0.9	93	N.D.
Cl^- (mg/l)	740	17.4	587	496
Total *P* (mg/l)	1.0	0.2	0.34	0.17
Water flux (l/m^2.h.bar)		8.1	13.3	15.7

rejections also for monovalent ions); alternatively, a multi-step configuration can be chosen with, e.g., UTC-20 or NTR 7450.

Buscio et al. [10] applied polyvinylidene difluoride (PVDF) ultrafiltration membranes to treat textile wastewater. A 90% COD removal, and 96% removal of C.I. Disperse Orange 30 and C.I. Disperse Rubine 73 was observed. This was claimed to be sufficient for water recycling, in spite of some remaining color. Membrane fouling, however, is a problematic issue. Zuriaga-Agusti et al. [11] applied a tubular ultrafiltration ceramic membrane in view of decreasing the fouling effect. The removal efficiency was 93%, which was thought sufficient. Their results have demonstrated that membranes with a larger pore size lead to more solutes to adsorb into the pores, which causes a sharp permeate flux decline due to the effect of pore blockage. Thamaraiselvan and Noel [12] reviewed potential strategies to overcome this fouling problem. In general, pretreatment stages may be necessary; modifying and optimizing the membrane separation process parameters such as feed composition, hydrodynamic conditions, and membrane properties could be a further method. This would also require developing new membranes and cleaning processes for fouled membranes.

In general, ultrafiltration is not considered sufficient for producing high-quality water, and rather applied as a pretreatment method. Arnal et al. [13] observed that the COD removal in ultrafiltration is not sufficient for directly reusing the permeate in the textile industry. On the other hand, they conclude that the permeate quality was optimal for using it as feed to a nanofiltration unit. Furthermore, the combined UF/NF process was found more efficient than NF as a stand-alone process, because fouling in NF was considerably reduced, while the total water recovery was higher. Similar observations were made by Simonic [14], who studied ultrafiltration as a pretreatment method for decolorization of residual dye-bath effluents after dyeing cotton/polyamide blends using reactive and acid dyes. The specific nature of the effluent determines the viability of ultrafiltration and/or nanofiltration. Van der Bruggen et al. [15] discussed the use of nanofiltration for the treatment of exhausted dye baths, and on the other hand, the use of ultrafiltration for the removal of spin finish from wastewater resulting from rinsing of textile fibers. Both applications are in principle feasible, but in practice the process is negatively influenced by membrane fouling.

Nanofiltration is often considered the optimal membrane process for textile effluents. It was applied on lab scale and pilot scale by Ong et al. [16], who found a removal of >90%, surprisingly close to what was obtained with ultrafiltration. In this case, however, salts are also removed (0% of NaCl and 90% of Na_2SO_4). A stable performance after several cycles of chemical cleaning was observed. Qin et al. [17] found a much higher dye removal, of over 99%. Turbidity, hardness, TOC and color of the treated water were less than 0.2 NTU, 60 mg/L as $CaCO_3$, 10 mg/L and 5 HU, respectively. They made a full study of all wastewater flows in a dyeing facility, and their study proves that 70% of the water can be recycled. The good performance of nanofiltration membranes was confirmed by several authors. For example, Hildebrand et al. [18] used typical polyamide membranes for removal of Remazol Turquoise Blue G, Remazol Yellow GR and Lanaset Blue 2R. Kurt et al. [19] also achieved a high COD, conductivity, and color removal efficiency using polyamide nanofiltration membranes in a pilot plant, and compared the results with reverse osmosis. Lau and Ismail [20] made an overview of various studies on nanofiltration for dye effluents, and remarked that while most conventional technologies seem unable to provide sufficient treatment for the effluents, nanofiltration membranes have a good performance, even though a compromise is to be made between dye rejection and permeate flux.

Fouling, however, remains a challenge. Chidambaram et al. [21] concluded that the effect of fouling is due to molecular membrane electrostatic interactions, acid–base interactions, and molecular size effects. The economics of the process are thought realistic when the performance of a nanofiltration unit remains unchanged for at least two years: an economic analysis [22] for remazol dye bath wastewater (which can be considered representative, since it contains high concentrations of NaCl reaching up to 80 g/l), calculated a payback period of less than 2 years assuming water recycling as a consequence of applying nanofiltration.

Depending on the type of the modules used, up to 80–90% of the process water can be recycled in a membrane filtration plant. Lower water recoveries can be chosen to obtain a more robust process; large values might cause problems with membrane fouling, so that more frequent membrane cleaning is necessary. Hollow fiber modules and spiral wound modules are more susceptible to fouling than, e.g., tubular membranes; the latter module type can be used to operate at relatively high recoveries.

13.3 Treatment Sequences

Today, the increase of human activities and water consumption by industries cause a decrease in water resources. Reuse of wastewater has gained importance due to reduction in water supply and increasing costs. Especially for the textile industry with high water consumption, it is possible to use treated water within the processes. Thus, it provides sustainable water management and protection of natural sources and also reduces the operating costs. Unfortunately, conventional treatment processes are not sufficient to provide effluent standards and required quality for water reuse. Based on this, membrane processes are known as the most promising technology which can guarantee high water quality. However, as already mentioned, membrane processes are faced with some operational problems such as fouling and concentrate stream which are known major obstacles for filtration processes. So, the reason behind the development of integrated membrane processes is to achieve better performance than stand-alone membrane processes. Weaknesses of existing membrane processes can be reduced by using integrated process [23].

As a further improvement over nanofiltration as such or with pretreatment, integrated membrane processes can be considered. Dasgupta et al. [23] give an overview of recent efforts to integrate or hybridize processes for treatment of textile effluents. Among the various proposed systems, the combination of physicochemical/biological and membrane separation processes is a logical choice. Integrated ozone oxidation with biological aerated filters [24] can be used to supplement membrane filtration. Coagulation is another possible way to enhance membrane filtration for textile effluents. For example, a combined system of coagulation and membrane processes was studied for reactive dyeing wastewater treatment, and when ultrafiltration was used, the hybrid system was found to be better not only in terms of permeate quality but also in fouling minimization [25]. *Moringa oleifera* could be a sustainable coagulant to do so [26]. Process integration with coagulation–flocculation may also be done by applying a coagulant on the concentrate from a filtration unit [27]. The outcome is shown in Fig. 13.1: the permeate is nearly colorless, while the treated concentrate has some remaining color, although much less than the original wastewater. Using nanofiltration, 82 and 67% removal of color and chemical oxygen demand (COD) from the colored wastewater was obtained, respectively; by coagulation–flocculation process with iron chloride/anionic polyacrylamide in a 8:1 ratio, 91% of color and 81% of COD from the concentrate stream was achieved.

Other hybrid systems were explored as well. One example is the use of a magnetic anion exchange resin prior to membrane filtration [28], which increased the permeate flux by 12.5% and reduced irreversible membrane fouling by 6.6%. Electrocoagulation was found to remove 37% of Direct Red Solophenyle 4GE, so that a combined process with nanofiltration would yield a colorless permeate [29]. A particular hybrid approach was used for treating highly alkaline textile mercerization wastewater: this comprised a pretreatment by microfiltration or ultrafiltration

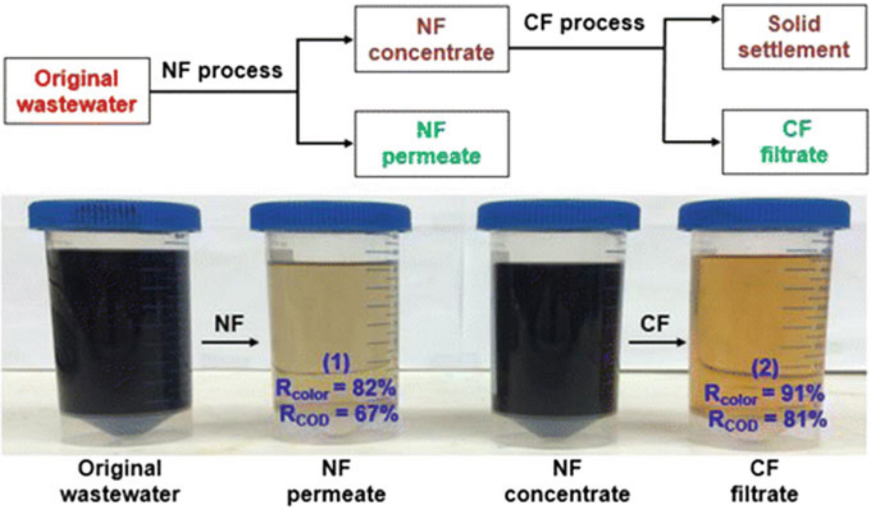

Fig. 13.1 Visual comparison of the original wastewater, the permeate from a nanofiltration unit, the concentrate from the same unit, and the concentrate after coagulation–flocculation. Reprinted with the permission from Ref. [27]. Copyright 2015 American Chemical Society

to remove turbidity and (some) organic matter, followed by nanofiltration for a complete (97–98%) COD removal. In this case, the permeate contains a high concentration of NaOH, which can then be recovered by evaporation (with a loss of only 12–17% in the nanofiltration stage) [30].

Finally, an obvious hybrid system is the membrane bioreactor, which has been studied extensively for application on textile processing wastewaters. It is evident that while such treatment may be effective, the only objective can be in water recycling; other components are degraded and therefore lost. Chamam et al. [31] studied a membrane bioreactor for removal of Cassulfon CMR, a sulphuric textile dye with a dark black-blue color used to dye jeans. In this case, direct membrane filtration was not sufficient, while the biomass had a high capacity to adsorb color (more than 4 g COD per g MLVSS), while the permeate had a COD below 60 mg/L. This approach has been studied in many cases; membrane bioreactors were also applied on pilot scale for textile effluents. For example, Yigit et al. [32] studied a pilot scale membrane bioreactor for highly concentrated mixed wastewater from wet processes (dyeing, finishing, and sizing) of a denim producing textile industry. Color values from as high as 8100 Pt Co levels were significantly reduced to about 50 Pt Co levels, indicating that MBR effluent could be reused in the production processes.

Biodegradation can be enhanced by optimizing the bioreactor. Such ‘enhanced membrane bioreactor’, consisting of two anoxic bioreactors followed by an aerated membrane bioreactor, a UV-unit and a granular activated carbon filter, was studied by Rondon et al. [33]. Once the biological system was acclimatized, 95% of dye, 99% of COD, 97% of nitrogen, and 73% of phosphorus were removed at a retention

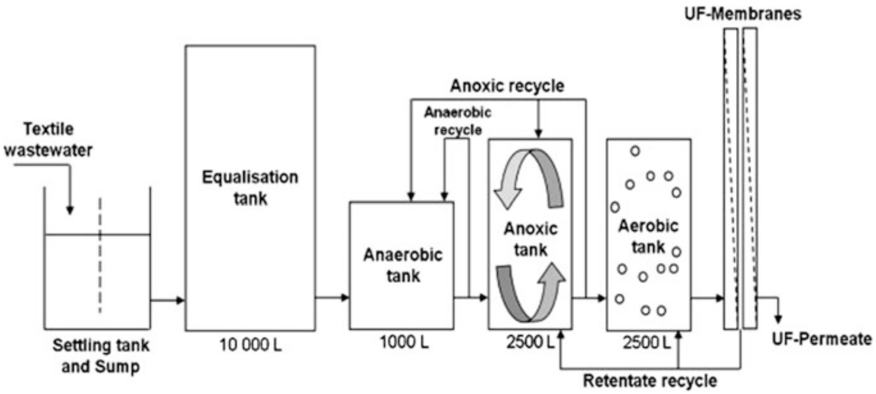

Fig. 13.2 A typical sequence for color reduction in textile effluent, comprising a combination of anaerobic–anoxic–aerobic degradation and a sidestream ultrafiltration. This system was tested at pilot scale. Reprinted with the permission from Ref. [37]. Copyright 2014 Elsevier

time of 74.4 h; after UV treatment and adsorption, color removal was complete. Other ways to improve biodegradation/removal were explored as well: the addition of powdered activated carbon [34], the use of white-rot fungus *Coriolus versicolor* to enhance the decoloration [35], and the use of anaerobic bioreactors [36]. The combination of anaerobic–aerobic reactors with membrane filtration can then be optimized to meet targets of color removal and COD reduction. A typical sequence is shown in Fig. 13.2 [37].

In all applications of membrane bioreactors, the aim is in water recycling; it can be concluded that this is viable and can be even considered state-of-the-art today.

13.4 Integrated Membrane Process

Textile wastewater treatment by membrane processes can be divided into two groups including stand-alone and integrated membrane processes. Integrated membrane processes have been defined as processes which include one membrane process combined with other conventional treatment technologies or a membrane pretreatment method [38]. Membrane processes have been used different applications including coagulation/flocculation [39–46]; combined membrane filtration [13, 47–52]; biological process [53–56]; electrocoagulation [57]; photocatalytic processes [58–63]; electro-catalytic oxidation [64]; advanced oxidation process [65]. Some of these integrated membrane processes used for treatment of textile wastewater aiming the various aspects including contaminant removal, water reuse, lower fouling, and higher permeate flux has been listed in Table 13.2. These integrated processes are designed to reach desired effluent standards or water quality besides reducing the limitations of the membrane processes. One of the

Table 13.2 Overview of various integrated membrane process studies carried out by different researchers

Integrated systems	Membrane characteristics	Wastewater characteristics	Removal efficiency	Permeate flux	References
Electro-Fenton process/MF – A laboratory-scale pilot – Dynamic cross-flow filtration TMP: 5 bar	Carbon graphite tubular membranes 14.4% porosity with a bimodal pore repartition (0.16 and 2.8 μm). The corresponding inner membrane area is of 23.4 cm^2	Acid orange 7	The abatement of the AO7 dye 96% after 60 min electrolysis	Steady-state permeate flux at 5 bar: 65.6 L/m^2 h	[66]
Homogenization–decantation/UF – Screening – Homogenization tank ($V = 200$ m^3, HRT: 2.5 days) – Cylindro-conical clarifier ($V = 18$ m^3) – Both laboratory plant and semi-industrial system – TMP 0.2 bar for both system	Hollow fiber membranes modules: U-1b pore size: 0.04 μm membrane surface: 0.5 m^2 U-4 pore size:0.03 μm membrane surface: 40 m^2 After each filtration process, the membranes were cleaned with a sodium hypochlorite solution (5 mg/L)	Dyeing process effluent COD: 806 mg/L Conductivity: 1825 μS/cm Color: 300 mg Pt-Co/L Cl^-: 270 mg/L SO_4^{2-}: 387 mg/L	Homogenization–decantation: color removal 17%, COD removal 10% combined lab plant treatment: color removal 30%, COD removal 66%. Combined semi-industrial plant treatment: color removal 33%, COD removal 60%.	Constant permeate flux at 10 L/m^2 h. The permeate reuse can save up to 13€ per 160 m of fabric produced	[67]
Photocatalytic oxidation process/UF/RO – 0.5 MPa for RO	– UF hollow fiber membranes (HAITAO) made of hydrophilic polyacrylonitrile (PAN) – RO membrane (VONTRON) made of polyamide	Simulated textile effluent COD: 247 mg/L Conductivity: 2360 μS/cm Congo Red: 40 mg/L Hardness: 740.74 mg/L pH: 4	Experimental results after photocatalytic oxidation process/UF/RO COD: 25 mg/L Conductivity: 88 μS/cm Congo Red: 0.32 mg/L $Hardness^-$: 28 mg/L	Photocatalysis as a pretreatment can reduce the membrane flux decline: for UF 12% for RO 8%	[63]
Coagulation unit/MF – Coagulant PACl – 7 min filtration and 3 min pause	– PE hollow fiber UF membrane – Total area 0.97 m^2 – MWCO 80 kDa Membranes were cleaned chemically by mixed solution of NaClO and NaOH (effective Cl 3000 mg/L, NaOH 500 mg/L)	Textile mill effluent COD: 413 mg/L Conductivity: 75 μS/cm Absorbance at λmax: 2.8 TSS^-: 125 mg/L TKN: 17 mg/L pH: 9.8	PACl dose 1.2 mmol/L, influent pH 5.5, HRT 3 h: – Color removed almost completely – COD removal 88%.	– Fouling is higher when the higher MWCO membrane was used – A more permeable filter cake was formed with PACl 1 mmol/L and could all decrease the membrane fouling effectively	[46]

(continued)

Table 13.2 (continued)

Integrated systems	Membrane characteristics	Wastewater characteristics	Removal efficiency	Permeate flux	References
Photocatalytic process/MF – TiO_2 photocatalyst, 18 W UV lamp, 0.5 L reactor volume – 0.5 g/L TiO_2 – Membrane module was immersed. Permeate was recycled back to the tank. 5 s backflushing. Bubbling of air 3 L/min	– Low-pressure submerged PP hollow fiber MF membrane – Membrane pore size: 0.1–0.5 µm – Membrane active surface area: 0.94 m^2	Acid Red 1 azo dye (AR1), Egacid Red G 200	– Decolorization efficiency 93.78% (c_{dye} = 15 mg/L, c_{TiO2} = 0.5 g/L, n = 400 rpm, T = 25 °C, λ_{UV} = 254 nm, I_{UV} = 62.9 m W/cm^2)	– Initial flux: For −25 kPa 100 L/m^2 h For −10.5 kPa 40 L/m^2 h For −5 kPa 20 L/m^2 h – Rapid flux decline was observed Because of TiO_2 particles – Sustainable permeate flux: 40 L/m^2 h	[61]
Photocatalytic process/NF – 5 L photocatalytic reactor batch and continuous model – A UV lamp (253.7 nm, 18 W) – 0.1–0.5 g/L of photocatalyst (ZnO)	– Polypiperazine amide NF membrane – MWCO 200 Dalton – Flat sheet membrane module, 9.8 cm × 9.8 cm × 5.1 cm	Congo red (CR) dye powder with a working solution of 20 mg/L.	– CR degraded after photocatalysis – For 0.1 g/L ZnO 23% – For 0.3 g/L ZnO 65% – For 0.5 g/L ZnO 44% – CR degraded after photocatalysis – For 0.1 g/L, 0.3, 0.5 g/L ZnO 100%	– 0.3 mg/L ZnO was the optimum dose for both flux decline and photodegradation – 0.1 mg/L ZnO was sufficient for photodegradation and 0.5 mg/L ZnO cause the overlapping and obstruction of UV light	[62]
Electro-catalytic oxidation/NF – Ti/SnO_2 – Sb_2O_3 electrode modified with rare element yttrium – Cross-flow membrane filtration module with	– PA NF membrane – An active membrane surface area of 13.85 cm^2 – MWCO 150–300 Da – 0.8 MPa operating pressure – The coupling system was cleaned by circulating 0.1% (w/v) NaOH solution and 0.1% (v/v) hydrochloricacid solution for 2 h per solution	– C.I. Acid Red73 (AR 73) wastewater – 0.5 g/L concentration	Retention of AR 73 molecules close to 99% by coupling process	Permeate flux values with max. cross-flow velocity or applied voltage of 5, 10 15 V were 3.2; 2.8; 2.45 L/m^2 h The total energy consumption was about 119.2 kWh/m^3 when the voltage was 10 V at a fixed operating pressure of 0.8 MPa	[64]

(continued)

Table 13.2 (continued)

Integrated systems	Membrane characteristics	Wastewater characteristics	Removal efficiency	Permeate flux	References
Ozone biological aerated filter (BAF)/UF/RO – Two-stage ozone-BAFs: eight primary ozone-BAFs and five secondary ozone-BAFs working in sequence-catalytic grain (with manganese oxide content of about 30%) and ceramic pellets – Four sand filters, two UF units and two RO units working in sequence	– PVDF UF with a total membrane area of 6160 m^2 – PA RO membrane with a total area of 10,500 m^2 – Alkaline detergents (30% caustic soda and 10% sodium hypochlorite solution) and acid detergents (20% citric acid and 30% hydrochloric acid) were used to wash the membrane units – Optimal cleaning frequencies for sand filters, UF and RO were 10 days, 40 min and 3 months, respectively	– A cotton textile mill effluent COD: 82–120 mg/L BOD_5: 12.6–23.1 mg/L SS: 38–52 mg/L Color: 32–64°	– Effluents with $COD \leq 40$ mg/L, $BOD_5 \leq 6.5$ mg/L, $SS \leq 15$ mg/L, $Color \leq 4°$ with optimal ozone dosage 20–25 mg/L – The total ozone consumption was about 0.4 kgO_3/kg $COD_{removed}$	– Permeation flux For UF 35–120 L/m^2 h – For RO 10–15 L/m^2 h – The running cost including electricity consumption (0.75 Yuan/kW), liquid oxygen cost and deterioration of the UF and RO membranes were 0.74 Yuan/m^3 for ozone-BAF and 1.61 Yuan/m^3 for membrane process, respectively. The production cost of permeate water was 2.35 Yuan/m^3	[56]
Coagulation–flocculation/NF – Aluminum sulfate '$Al_2(SO_4)_3$ 16 H_2O' as coagulant and an anionic polyelectrolyte type Magnafloc 919 as flocculant-optimum dosages were 0.8 and 0.9 g/L for coagulant and 3.4 mg/L for flocculant – TMP 10 bar for NF	– Spiral wound NF membrane with a total area 0f 2 m^2, 200 Dalton – Membrane cleaning steps: (1) with water (2) with NaOH 2% for 45 min (3) rinsing with distilled water (4) with nitric acid solution 2% for 30 min (5) rinsing with distilled water	– A textile factory effluent COD: 227–627 mg/L Conductivity: 3.59–4.5 mS/cm TDS: 1.79–2.26 g/L Turbidity: 31–85 NTU	Color, COD and salinity removal efficiencies 100, 60, and 35%, respectively	– Average permeate flux at steady state of 28 L/h.m^2	[45]

(continued)

Table 13.2 (continued)

Integrated systems	Membrane characteristics	Wastewater characteristics	Removal efficiency	Permeate flux	References
MF/NF – TMP 12 bar for NF	– MF tubular membrane: total area of 0.155 m^2, 0.1 µm pore diameter, aluminum material – NF spiral membrane: polyamide, total area of 2.5 m^2, 150–300 Dalton	– A textile factory specialized in the dyeing of cotton fabric – Effluent 1: COD: 2450 mg/L Cl^-: 21.3 g/L TDS: 11.42 g/L Color: 3.88 Abs pH:10.65 – Effluent 2: COD: 2160 mg/L Cl^-: 11.71 g/L TDS: 9.54 g/L Color: 2.05 Abs pH: 9.23	– COD removal 73.5% for Effluent 1 and 80.2% for Effluent 2 Color removal 96% for effluent 1 and 98.3% for effluent 2 – Salinity removal 37% for effluent 1 and 45% for effluent 2	Steady state flux – 30 L/h.m^2 for effluent 1 – 40 L/h.m^2 for effluent 2 – MF as a pretreatment – Limit the effect of fouling – Prevent to obstruction – This membrane combination can save 50% of the wastewater and 30% of quantity of salt used	[52]

limitations of the membrane processes is membrane fouling which cause to increase the maintenance cost of the membrane and membrane life time. Researchers claim that membrane fouling can be overcome by using different pretreatment technologies. For instance, as previously discussed, ultrafiltration (UF) as a pretreatment process for NF was investigated by Arnal et al. [13] in the reuse of the secondary effluent of textile wastewaters from different processes of textile industry. It has been reported that treatment of textile wastewater by the combined UF/NF processes reduced the membrane fouling and also increase the water recovery rate compared to the processes that use NF membranes alone.

In another study by Simonic and Lobnik [44], the efficiency of a hybrid flocculation/UF process for a real dye-house effluent was investigated with or without a flocculation pretreatment using hydrophilic and hydrophobic membranes in order to reduce the fouling and to compare the performances of these membranes. So, alum as a coagulant and a cationic polyelectrolyte as flocculant were used in order to provide higher permeate flux by the removal of surfactants. The results showed that cationic flocculant reacted with disperse water soluble dyes which have anionic characteristic and anionic surfactants in the solution to form flocs. Higher flux and lower membrane fouling was observed when the UF follows the flocculation for PVDF membrane. A representative schematic diagram of hybrid coagulation–flocculation/membrane process is shown in Fig. 13.3 [42].

Biological treatment/membrane process combinations have been used for a long time to examine the efficiencies of these processes for textile wastewater treatment. For instance, a comparative study was performed between direct NF and UF/NF hybrid systems by Debik et al. [54] for evaluating the performances in aerobically and anaerobically pretreated textile wastewater. It was observed that UF/NF membrane combination led to achieve higher permeate flux compared to NF membrane alone. Also, the results highlighted that the permeate quality of aerobically pretreated wastewater was better than the permeate quality of the raw wastewater and anaerobically pretreated wastewater. A similar research by Zuriaga-Agustí et al. [55] was carried out for the reuse of textile wastewater as

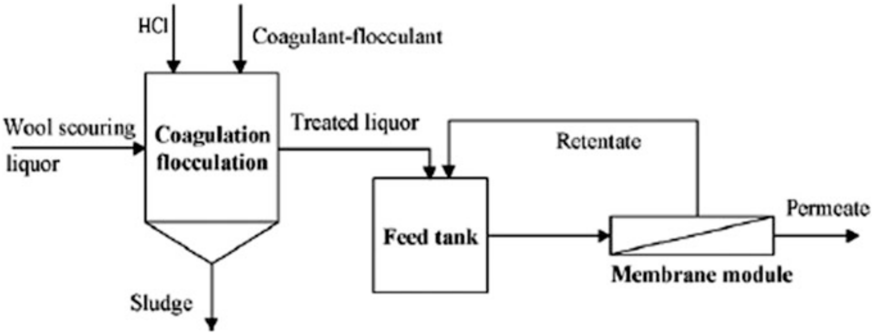

Fig. 13.3 A schematic diagram of the typical hybrid coagulation–flocculation/membrane process. Reprinted with the permission from Ref. [42]. Copyright 2008 Elsevier

process water by a hybrid process combining a sequencing batch reactor (SBR) process with NF membranes. The study also aimed to evaluate the color removal efficiency in the SBR and the influence of the addition of NF retentate on the SBR feed. Color removal efficiencies reach to 90% for the red and blue 75% for yellow when the SBR feed was only the textile synthetic wastewater which containing three different reactive dyes. However, when the SBR feed was the mixture of 1:1 synthetic wastewater and NF rejection the color removal efficiency was reduced 10–15%.

Recently, many researchers focused on the potential of combined catalytic and membrane separation processes such as photocatalytic, electrocoagulation, Fenton oxidation, and Electro-catalytic processes. Application of the hybrid membrane photocatalytic reactor (MPR) was evaluated by Damodar et al. [58] for the degradation of reactive black 5 (RB5) dye and the effect of initial dye concentration on energy consumption per amount of dye removed. 82–100% color, 45–93% TOC, and 50–85% COD removal were achieved at hydraulic retention time (HRT) of 4 h by MPR reactor consisting of two Hg UV-C lamps (15 W, 254 nm) and one flat plate polytetrafluoroethylene (PTFE) MF membrane module. A similar photocatalytic membrane reactor for degradation of textile wastewater was used in different studies and one of them is shown in Fig. 13.4 [62]. Different advanced oxidation processes have been also combined with membrane processes. It is a case in point, combined Fenton oxidation and membrane bioreactor process was investigated by Feng et al. [65] for the advanced treatment of textile dyeing effluent.

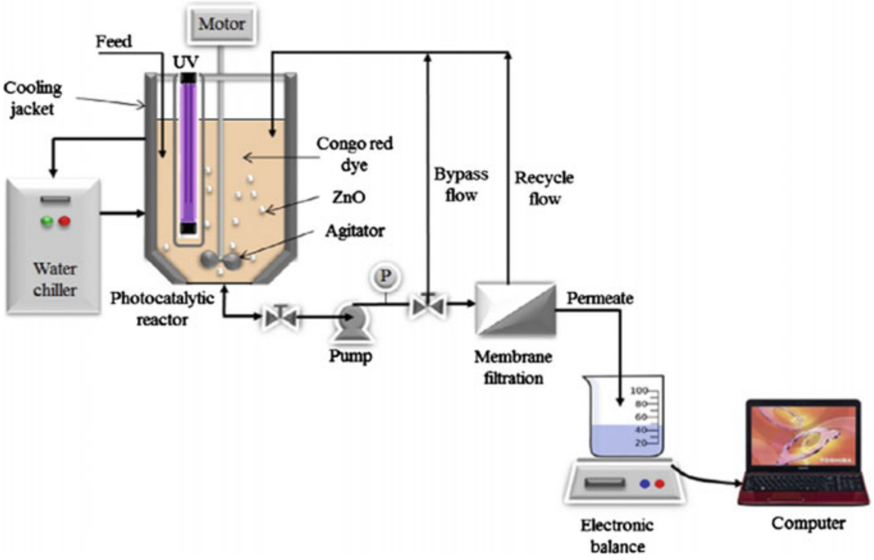

Fig. 13.4 A typical schematic diagram of the laboratory-scale membrane photocatalytic reactor. Reprinted with the permission from Ref. [62]. Copyright 2014 Elsevier

A general conclusion has been attained from studies focused on the use of integrated membrane processes used for the treatment of textile wastewater. The studies concluded that integration of conventional treatment technologies with membrane processes appears to be very attractive to reuse of textile wastewater and to overcome weaknesses of membrane processes.

13.5 Concentrate Treatment

Membrane processes play an important role in wastewater treatment as an effective technology for wastewater treatment and recycling in different industrial activity by providing high-quality water. Formation of membrane fouling and production of concentrated streams are limited to membrane performance, process sustainability, and economy. Textile effluents contain high concentrations of organic components (dyes and additives) and inorganic components (salts). The permeate stream can usually be reused as a process water; the concentrate is a highly colored waste stream with a high concentrations of organic and inorganic compounds. Recycling of dyes or other chemicals is generally not possible because the composition of the concentrate is too complex. Direct discharge is also not possible due to the composition of the concentrate. Color can be removed partially from the concentrate in an activated sludge system because many dyes are not biodegradable [68]. Consequently, concentrate stream in textile wastewater treatment is a major obstacle for application membrane processes.

Different application areas such as brackish water, seawater, etc., for the treatment of membrane concentrate has been focused on in the literature. Unfortunately, there are fewer publications related to the textile membrane concentrate. The application possibilities for textile wastewater concentrate generally focused on decreasing the production of concentrate stream or returning the concentrate stream to feed. Different technologies can be used for the treatment of textile membrane concentrate considering the characterisation of concentrates. Table 13.3 lists the various treatment applications for textile concentrate, involving one or more treatment techniques which address the different membrane concentrates. Also, Fig. 13.5 illustrates the flow diagram of integrated process for the treatment of RO rejects [69]. In this study, capital cost for ED system was found to be 1968.75 US \$. Assuming the membrane life to be 5 years, the total operating cost of ED process for treating 1.5 m^3/h of feed was calculated to be 0.133 US \$/m^3. The calculated overall cost of evaporation process alone to treat RO reject was found to be 3.88 US \$/m^3. Combination of ED process and evaporation decreased the volume load on the evaporator and consequently resulted a reduction in the operating cost. The cost of decarbonization of RO reject for pretreatment of the feed to ED was calculated to be 0.04 US \$/m^3. Therefore, the overall operating cost of ED-evaporation integrated process is 0.55 US \$/m3 compared to 3.88 US \$/m^3 incurred when only evaporation is employed. Thus, it was stated that the integrated process provides a very

Table 13.3 List of various treatment applications for the treatment of textile concentrates

Treatment technology	Concentrate characteristics	Removal efficiency	References
Ozonation/aerobic treatment – A reaction column for ozonation having 20 cm diameter with 102 cm height – Bioreactor with 5 L working volume – Granular sludge	Textile mill effluent NF270 concentrate DCOD: 3000–4300 mg/L Conductivity: 13.72 mS/cm pH: 8.80–10.5 BOD_5: 345–2303 mg/L SO_4^{2-}: 395–580 mg/L SS: 6618–12,200 mg/L	– Biodegradability of the membrane concentrate was almost three times increased by the ozonation with concentration of 130 mg/Lmin. – DCOD, BOD_5 and SO_4^{2-} removal efficiencies lower than in the first 10 days, after 10 days increased to over 80%.	[71]
Electrodialysis/Evaporation – 10 L capacity, the stack consists of five cell pairs, 6 cation transfer membrane, 5 anion transfer membrane	RO reject of textile effluent COD: 6700 mg/L Conductivity: 62.6 mS/cm TDS: 47,000 mg/L pH: 8.8 BOD: 2500 mg/L SO_4^{2-}: 2750 mg/L Cl^-: 16,500 mg/L	– ED concentrated RO reject of textile industrial effluent from 4.35 to 24% inorganic constituents – ED can be reduced the volume of textile effluent reject being sent to the evaporator enormously – 1 m^3 of textile RO reject was 0.55 US $ – Evaporation alone cost was 3.88 US $	[69]
Fenton like reactions – Batch reactor in the dark and under visible light – H_2O_2 alone and Nafion-Fe^{+3}/H_2O_2 as an immobilized Fenton reagent	Membrane concentrate from nanofiltration of biologically treated secondary textile effluent	– Nafion/Fe^{+3} system kinetically faster and more complete oxidation than H_2O_2 alone – Reduction of 50% in TOC and 20–50% in optical absorbance after 3 h	[72]
Ozonation – O_3 concentration: 12 ppm over 120 min	Real NF membrane concentrate COD: 595 mg/L Conductivity: 5 mS/cm TOC: 190 mg/L BOD_5: 0 mg/L pH: 7.9	– BOD_5 increase from 0 to 75 mg/L – COD removal was 50% – TOC removal was 30%	[73]

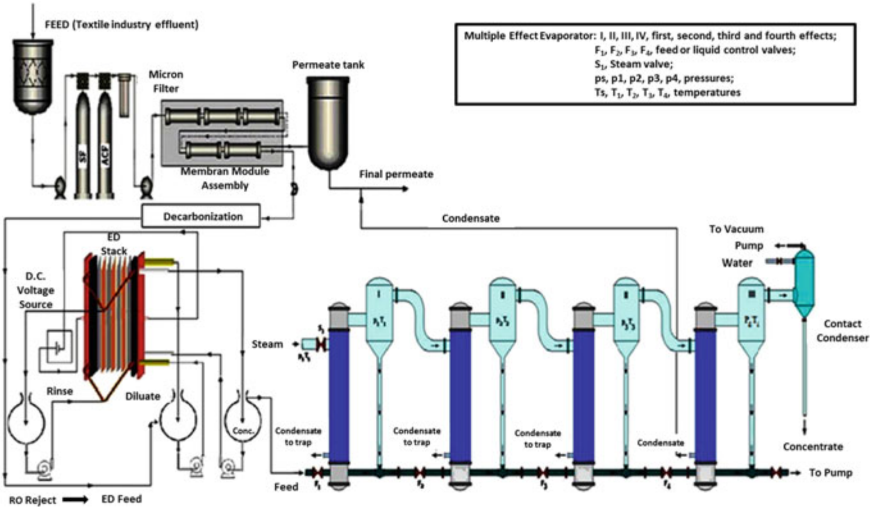

Fig. 13.5 A process flow diagram of integrated process for treatment of RO reject. Reprinted with the permission from ref [69]. Copyright 2014 Elsevier

economical solution when the RO reject is treated by ED before carrying out evaporation [69].

Many of the investigations focused on physicochemical process for treatment of highly concentrated stream. For instance, Forward osmosis (FO)-Coagulation/Flocculation (CF) hybrid process has been developed by [70] to offer an alternative technology for the effective treatment and reuse of textile wastewater. FO process was used to dewater the textile effluent; CF was applied to FO highly concentrated stream for dye precipitation and removal with high efficiency and low chemical dosages. After FO process, the dye concentration in the stream increased by about 10 times. It was observed that CF can remove more than 95% of the dyes with a small dosage of coagulants and flocculants at 500–1000 ppm, effectively.

13.6 Resource Recovery from Textile Wastewater

Nanofiltration membranes are semipermeable with a pore size from ~0.5 to 2.0 nm in diameter, which lies between the typical values found in ultrafiltration and conventional reverse osmosis membranes [74]. This provides an excellent opportunity for fractionation of different solutes, allowing salts to partially pass through the membrane and retaining molecules with larger size, based on the mechanisms of sieving effect as well as Donnan (electrostatics) repulsion for ion fractionation [74]. Due to these unique properties, NF membranes have been applied to separate organic solutes/salt mixtures (examples including separating pharmaceutical compounds [75–79], glyphosate [80], saccharides [81], heterocyclic drug derivatives [82], and other organic acids from salty aqueous solutions [83].

By retaining organic compounds (dyes) and allowing salts to pass, a brine solution is obtained that may be further desalted, so that water, salts, and dye compounds can all be recycled, which goes beyond a simple water recycling purpose. Table 13.4 summarizes (some of) the investigations in view of such fractionation carried out by different researchers on the treatment of textile effluents using typical commercial NF membranes; in Table 13.5, an overview is given of the performance of lab-made membranes.

For example, asymmetric cellulose acetate NF membranes achieved >99.0% rejection for five reactive dyes (i.e., reactive orange 12, reactive red 24, reactive black 5, reactive blue 74 and reactive blue 13) and moderate salt rejection ($\sim$10% for 30 g/L NaCl solution; $\sim$40% for 10 g/L Na_2SO_4 solution) [84]. Similarly, the commercial DK (Osmonics) NF membrane was investigated for reactive dye desalination and purification, in view of water recycling. Above 96.0% rejection for reactive black 5 and 21.1% rejection for the salt was observed [101]. Furthermore, the application of the commercial DK 2540F NF membrane with MWCO of $\sim$300 Da in the treatment of real dye bath streams (direct dyes and reactive dyes contained) illustrated that NF membrane can completely remove the dyes with 47–52% salt rejection [90]. The unsatisfying fractionation of dye/salt mixtures for these commercial dense NF membranes is due to the high salt content that remains in the feed. Simultaneously, these NF membranes also suffer a high risk of flux decline. Van der Bruggen et al. [88] demonstrated that a high salt content in the feed solution results in a dramatic decrease of the membrane flux due to a higher osmotic pressure, which may strongly limit the applicability of NF technology for direct treatment of dye baths.

On the basis of a comprehensive physicochemical characterization, it was concluded that loose poly(piperazineamide) based NF membranes, namely Sepro NF 6 and NF 2A with a corresponding MWCO of 862 ± 80 Da and 493 ± 53 Da, can be an alternative to the commercial dense membranes for the fractionation of organic matter/NaCl mixtures. Sepro NF 6 and NF 2A membrane have a salt transmission of 88.9 and 67.3% for a 0.01 mol L^{-1} NaCl solution with relatively high permeate flux. Furthermore, the superhydrophilicity of these two loose NF membranes shows their high potential to reduce fouling [102].

The combination of a high salt transmission (over 95.2% in 40 g L^{-1} NaCl solution) and an almost complete dye retention for the two studied loose NF membrane allows for an effective fractionation of dye/NaCl mixtures, which can facilitate brine reuse for FO and BEMD application and dye recovery from textile wastewater [103]. The diafiltration of a direct red 80/NaCl mixture with 20 g L^{-1} NaCl by Sepro NF 2A and NF 6 underlines the excellent desalination capacity of loose NF membranes: 95.5 and 96.6% of salt is removed from the mixture liquor, respectively. Additionally, the NaCl salt remains slightly concentrated when the post-concentration of the dye solution is performed at a factor of around 4.0. However, cake-enhanced concentration polarization can significantly lower the

Table 13.4 Performance of typical commercial NF membranes for textile wastewater treatment in view of fractionation

Membrane (MWCO)	Dye	PWP[a] (L m^{-2} h^{-1} bar^{-1})	Dye rejection (%)	Salt rejection	References
Cellulose acetate NF membranes (–)	Reactive orange 12	8.1 at 25 °C	99.9	37.7% for 10 g L^{-1} NaCl	[84]
	Reactive red 24		99.93		
	Reactive black 5		99		
	Reactive blue 74		99.93		
NFT-50 (159 Da)	Reactive blue 19	8.5 at 25 °C	99.4	~80% for Na^+ in feed (1.1g L^{-1} $NaHCO_3$; 0.56g L^{-1} Na_2CO_3)	[85]
	Reactive orange 12		99.6		
	Reactive red 24		99.7		
	Reactive black 5		99.9		
DS5 DK (150–300)	Reactive black 5	6.60 at 25 °C	99.5	~20% for 10g L^{-1} NaCl at 8 bar	[86, 87]
	Reactive blue 19		99.7		
UTC-60 (~150 Da)	Reactive orange 16	10 at 25 °C	97.9	30.1% for 0.58g L^{-1} NaCl	[88, 89]
	Reactive blue 2		99.9%		
DK 2540F (~300 Da)	Mixed yellow S3RS, red SB and blue BFS	4.0 at 30 °C	~100	~30% for 5.8g L^{-1} NaCl	[90]
TFC-SR2	Reactive black 5	17 at 25 °C	98	12% for 10g L^{-1} NaCl	[91]
NF 270 (~300 Da)	Amido black 10 V	14.5 at 25 °C	~100	20% for 2g L^{-1} NaCl	[92, 93]
NTR-729HF	Reactive red (Benefix)	7.2 at 35 °C	82.5	54.1% for 10g L^{-1} NaCl	[94]

[a] PWP denotes pure water permeability

Table 13.5 Performance of lab-made NF membranes for textile wastewater treatment in view of fractionation

Membrane (MWCO)	Dye	PWP[a] (L m^{-2} h^{-1}·bar^{-1})	Dye rejection (%)	Salt rejection	References
Tubular ceramic-based multilayer NF membranes (-)	Congo red	~9 at 25 °C	97.6	2.2% for 5 g L^{-1} NaCl	[95]
	Methylene blue		99.8		
Hollow fiber membranes coated with sodium carboxymethyl cellulose (~700 Da)	Congo red	7.0 at 25 °C	99.90	5% for 6 g L^{-1} NaCl	[96]
	Methyl blue		99.75		
	Sunset yellow		82.2		
Hollow fiber NF membrane by UV-photografting using sodium *p*-styrene sulfonate (~2000 Da)	Acid orange 10	4.0 at 25 °C	98	7% for 9.95 g L^{-1} NaCl	[97]
Hollow fiber NF membrane by UV-photografting using sodium *p*-styrene sulfonate (~4600 Da)	Direct yellow 8	15.0 at 25 °C	99.8	3% for 9.95 g L^{-1} NaCl	[97]
	Reactive orange 16		94.0		
	Acid orange 10		96.4		
Ultrathin graphene nanofiltration membrane	Direct red 81	3.26 at 25 °C	99.9	~41% for 1.17 g L^{-1} NaCl	[98]
	Methylene blue		99.8		
Positively charged PA6DT-C NF membrane	Methylene blue	13.5 at 25 °C	97.1	~20% for 1.62 g L^{-1} NaCl	[99]
NF membrane through polymerization of polyethyleneimine and isophthaloyl chloride	Safranin O	4.9 at 25 °C	99.8	85% for 0.058 g L^{-1} NaCl	[100]
	Orange II sodium		98.75		
Polyamide-imide hollow fiber nanofiltration membrane	Reactive blue 9	6.0 at 25 °C	99	~25% for 0.5 g L^{-1} NaCl	[16]
	Reactive black 5		99		
	Reactive yellow 81		99		

permeate flux of loose NF membranes, requiring a new strategy to mitigate this phenomenon for flux enhancement during diafiltration.

Generally, the negative charge carried by the commercially loose NF membranes (Sepro NF 6 and NF 2A) allows for high rejection of divalent salts (i.e., Na_2SO_4), which limits the effective fractionation of dye/Na_2SO_4 mixtures and increase the water consumption if diafiltration is applied. Specifically, a tight polyethersulfone UF membrane (i.e., UH004) with a MWCO of 4700 Da was found to offer a new opportunity for the separation of dye/Na_2SO_4 mixtures. The UH004 membrane allows for an almost complete penetration of Na_2SO_4. Due to a combination of dye aggregation, which increases the effective size of the dyes, and electrostatic exclusion of the negatively charged dyes from the negatively charged pores of the UH004 membrane, a high rejection (>98.9%) of dyes can be obtained, indicating the high feasibility for the fractionation of dye/Na_2SO_4 mixture. The ultrafiltration-diafiltration process for dye/Na_2SO_4 mixtures containing 55 g L^{-1} Na_2SO_4 shows nearly 97% removal of Na_2SO_4 and a low dye loss (<3%).

However, in wastewater treatment, the application of polyethersulfone (PES) UF membranes is limited by the occurrence of membrane fouling, which reduces the permeate flux and deteriorates the effluent quality. The incorporation of nanoparticles (i.e., nano-WS_2 and Stöber SiO_2) with ultralow amount was found to enhance the permselectivity and alleviate membrane fouling [104]. 0.10% (WS_2/PES) nano-WS_2 and 0.30% (SiO_2/PES) Stöber SiO_2 are the critical concentrations of nanoparticles doped in the PES polymer matrix to improve the membrane permeability. However, beyond these critical concentrations of nanoparticles, pore blocking in the PES membrane is observed, which reduces the membrane flux.

Thus, novel membrane technologies (i.e., loose NF membranes and tight UF membranes) are proven to effectively fractionate dye/salt mixed solutions, which can be an alternative to dense NF membranes for the treatment of textile wastewater.

The fractionation approach may be even more elaborated. The objective of achieving an integrated zero discharge system was already suggested on the basis of a combination of chemical, biological, and membrane processes [101]. Van der Bruggen et al. [8] proposed an integrated system for zero discharge, with full recycling of all components in wastewater (apart from reuse of dyes, which was not considered). This is shown in Fig. 13.6.

After an initial pretreatment by microfiltration, the separation between organic compounds, which have to be retained by the membrane, and the water with dissolved salts, which should permeate through the membrane, is as before. As observed, this separation is only to a limited extent possible with conventional membranes, since high rejections for bulk organics entail significant rejections of dissolved ions, which is to be avoided here. Selective rejection of organic compounds can be achieved through the development of tailored membranes, with the ambition of achieving a 90% rejection of organics, while recovering 90% of inorganics in the permeate.

The retentate fraction of the first nanofiltration unit is a concentrated organic solution; when the treatment is operated at elevated temperature, this can be validated in a membrane distillation (MD) step, where the organic fraction is separated

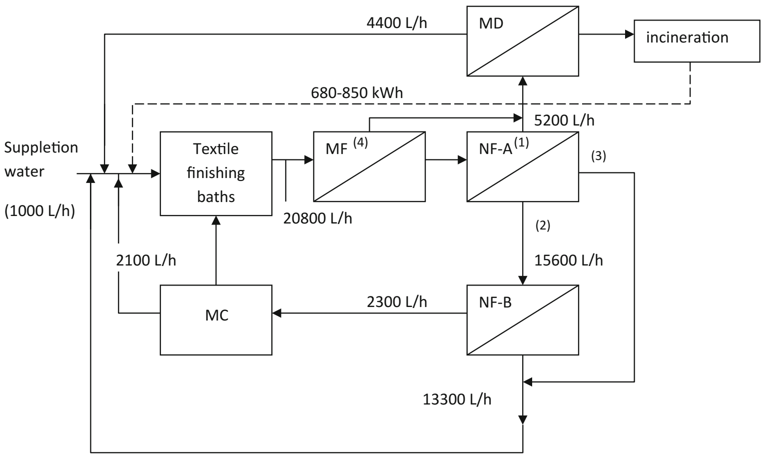

Fig. 13.6 Integrated membrane-based water treatment system for treatment of textile wastewater [8] (*full line* water stream; *dashed line* energy stream; *MD* membrane distillation; *NF* nanofiltration; *MC* membrane crystallizer). Reprinted with permission of Elsevier. *1* To be replaced by UF in the case of sulfur dyeing, disperse dyeing and pigment dyeing; *2* for reactive dyeing, metal-complex dyeing, mordant dyeing; *3* for vat dyeing and other techniques where no salts are used; 4 *o*perated in dead-end

from the water. The distillate is recycled to the finishing process; the remaining organic fraction has an added value by utilizing its energy content in an incineration process. The energy yield may make up for the loss of energy by losses in the different treatment steps. However, this would not allow to recycle dyes, as proposed above.

The retentate fraction of the second nanofiltration unit is a brine, from which crystals should be produced. Membrane crystallizers have been shown to yield crystals with a remarkable purity, and will be used here as a means for valorization of crystals obtained from the reverse osmosis concentrates. In doing so, it may be possible to provide added value to the production of salt crystals, which are generally not very high in value. However, by changing the conditions in the crystallizer, it is possible to selectively obtain a given salt with high purity, which may have economical value.

Simulations [8] show that this proposed concept of an integrated membrane-based system to treat wastewater of the textile finishing industry is feasible. Recycling of water obtained in nanofiltration, membrane distillation, and membrane crystallization, of energy (intrinsic energy content of recycled water and from combustion) and of materials (salts from membrane crystallization) can be realized; furthermore, although the dyes are not reusable in this concept as dye compounds, their caloric value is exploited. The only waste streams generated by the system are the ashes from the incineration unit, and small rinsing streams for the membrane units.

Since the publication of the scheme shown in Fig. 13.6, research on process intensification in the textile industry has substantially increased [105]. The concept of process integration is accepted today, but apart from some exceptions, not yet applied in wastewater treatment. Tahri et al. [52] used microfiltration combined with nanofiltration in order to reuse the treated water of selected dyeing baths in the dyeing process. A comparable membrane-based treatment strategy using dead-end microfiltration with a 5 μm filter to remove coarse particles and to minimize fouling of further NF and RO membranes was developed by Uzal et al. [106] for the possible recycle of indigo dyeing wastewater to the process itself. Compared to the flowsheet shown in Fig. 13.6, this represents the two first processes. This should be considered today's standard in advanced textile wastewater treatment [105]. Vergili et al. [107] came even closer to Fig. 13.6, by adopting the zero liquid discharge (ZLD) concept in treating textile dye bath wastewater via integrated membrane processes. This integrated process included different combinations of ultrafiltration, loose nanofiltration, tight nanofiltration, and reverse osmosis. The authors concluded that it is both technically feasible and economically viable. Other approaches still rely on biological processes, which implies that sludge is generated, and a fully closed cycle can therefore not be obtained. Resource recovery in this context could comprise the use of wastewater as an energy source [108]. The difficulty is that a system without biological treatment requires the development and use of new separation or transformation processes. This should be (a) a separation more selective than can be achieved by conventional processes, (b) which would not generate waste by-products, and (c) allows a full integration of all process streams including recycle streams.

Using bipolar membrane electrodialysis (BMED), brines can be separated into acids and bases. This may be an option for replacement of the membrane contactors: the use of bipolar membrane electrodialysis with filtration by a loose NF membrane can facilitate the extraction of dye and the regeneration of pure water, acid, and base from textile wastewater, in view of zero liquid discharge [109].

13.7 Future Perspectives

The textile industry is changing to a new interpretation of use of resources. Water is a key factor in this industry due to its large consumption, the reason why a natural evolution of strategies has taken place over time. First, water treatment was the only necessity in order to meet regulations. Water reuse was then considered as a real option to minimize water consumption. Nowadays, the economic and environmental potential of the recovery of dyes and salts is on the table. A zero discharge approach is persecuted and efforts are mainly addressed toward this objective. Recycling of water while recovery the different compounds in the wastewater is currently technically and economically viable. Thus, the textile industry is facing dramatic changes in the way in which a process is considered. What in the past was considered a residual stream and consequently a problem, now has become a source of valuable material (dyes, salts and water) and hence an opportunity. This has and is being possible thanks to the introduction of novel membrane technology that allows a dual objective: recovery of dyes, salts and water, and energy reduction.

Nanofiltration has already shown a clear capacity of treatment and a very good production of high-quality water, and it is considered as one of the most attractive technologies for dyes and water recovery. Nanofiltration membranes can retain ions and small organic molecules from an aqueous solution, which is required if dyes fractionation and water recovery is aimed. The main challenge that is still keeping busy many researchers is the presence of salts, which leads to several operating problems such as fouling, salt deposition, high osmotic pressure, etc. Nanofiltration may be studied as stand-alone technology but also integrated in hybrid systems in order to take advantage of different technologies working together. The combination of reaction and separation is a typical example but normally leads to the degradation of compounds, thus, the system aims at the elimination of compounds but not at the recovery. The recent research discussions are moving to another direction: zero discharge. This means that everything that is in the wastewater is considered as a source of valuable compounds (including water as the main one) and therefore, it should be recovered. To achieve this, a final approach is water fractionation. The selective separation of each compound and the final recovery of pure water is the main objective. Thus, a zero discharge process is obtained. Typical dense nanofiltration membranes find difficulties to separate the different compounds of the organic fraction, leading to a retentate that consists of a mixture of organic compounds without any value of application. Loose nanofiltration and tight nanofiltration membranes are the ones that can solve this difficulty since they have already proved effectively the fractionation of dye/salt mixed solutions. These membranes are still under research but we will not have to wait for too long to have them in the market. Efforts should be focused then on the industrial implementation of this technology in terms of membrane development as well as process design. Some results on the implementation of technology for reusing water in the textile industry have been already shown a clear advantage compared to a lack of action. For instance, the WASATEX project (www.wasatex.eu) is based on the first textile wastewater plant that integrates several membrane operations (membrane bioreactor + reverse osmosis + nanofiltration + OX system). The obtained results show figures of great interest: the yearly net saving cost is 386,333.9 €/year. In addition, other savings are envisaged: water saving of 306,000.0 m^3/year; natural gas saving of 549,700.6 Nm^3/year; and, CO_2 emissions saving of 1.251,1 ton/year. With these values, betting on the application of a treatment system is more than advisable since the economic benefit is a big support of this environmentally friendly approach.

13.8 Conclusions

The textile industry is facing new challenges related to the reuse of water since an approach of using fresh water is not anymore acceptable. The quantity and quality of water have to be satisfied, involving demanding standards. Thus, treatment of wastewater must lead to high-quality water and, if possible, to the recovery of the present compounds (dyes and salts, normally). Nanofiltration is the core technology proposed to achieve this target and provide with solutions to the textile industry. Nanofiltration is characterized by a high solvent permeability, easy scale-up and easy chemical cleaning. Thus, introducing this technology into the industrial scenario seems a very realistic approach. The quality of the NF permeate is comparable to typical groundwater in hardness (~40 mg/L Ca or 10 °F), concentration of organic compounds, and turbidity. Fouling, however, remains a challenge. The effect of fouling is due to molecular membrane electrostatic interactions, acid–base interactions, and molecular size effects. Thus, in many cases, ultrafiltration is applied as a pretreatment method. The COD removal in ultrafiltration is not sufficient for directly reusing the permeate in the textile industry but it can be used as feed to a nanofiltration unit. Furthermore, the combined UF/NF process has been found more efficient than NF as a stand-alone process, because fouling in NF was considerably reduced, while the total water recovery was higher. The economics of the process are thought realistic but only if the performance of a nanofiltration unit remains unchanged for at least two years.

As a further improvement over nanofiltration as such or with pretreatment integrated membrane processes (pretreatment by microfiltration or ultrafiltration to remove turbidity and some organic matter, followed by nanofiltration for 97–98% COD removal) can be considered. Integrated membrane processes have been defined as processes where membrane operations are combined with other conventional treatment technologies or a membrane pretreatment method. Several hybrid processes for treatment of textile effluents have been identified: the combination of physicochemical/biological and membrane separation processes; integrated ozone oxidation with biological aerated filters; coagulation; magnetic anion exchange resin prior to membrane filtration; electrocoagulation; membrane bioreactor; combined catalytic and membrane separation processes such as photocatalytic, electrocoagulation, Fenton oxidation, and Electro-catalytic processes. But in many of these systems the ‘pollutants’ are degraded and therefore lost.

Recovery of both water and components should be considered always as the main objective to be achieved. In this sense, novel membranes (i.e., loose NF membranes and tight UF membranes) are proven to effectively fractionate dye/salt mixed solutions, which can be an alternative to dense NF membranes for the treatment of textile wastewater. The fractionation approach leads to a zero discharge system. An example is shown in this book chapter with full recycling of all components in wastewater (apart from reuse of dyes, which was not considered), including: (i) an initial pretreatment by microfiltration; (ii) the separation of organic compounds, which have to be retained by the membrane, from the water with dissolved salts, which should permeate through the membrane; (iii) the retentate fraction of the first nanofiltration unit is a concentrated organic solution; when the treatment is operated at elevated temperature, this can be validated in a membrane distillation (MD) step, where the organic fraction is separated from the water; (iv) the distillate is recycled to the finishing process; (v) the remaining organic fraction has an added value by utilizing its energy content in an incineration process; (vi) the retentate fraction of the second nanofiltration unit is a brine, from which crystals should be produced; (vii) membrane crystallizers could be used as a way of valorization of crystals obtained from the reverse osmosis concentrates.

Integrated membrane-based systems to treat wastewater of the textile finishing industry are thus feasible. Recycling of water while recovery the different compounds in the wastewater is technically and economically viable. Efforts should be now oriented toward the industrial implementation of this technology in order to reach the sufficient maturity and experience to consider it a common part of the operation units in the textile industry.

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In the original version of the book, belated corrections in figure captions of Figs. 3.14 and 3.16 have to be incorporated in Chap. 3. The erratum chapter and the book have been updated with the changes.

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