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

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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

[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].

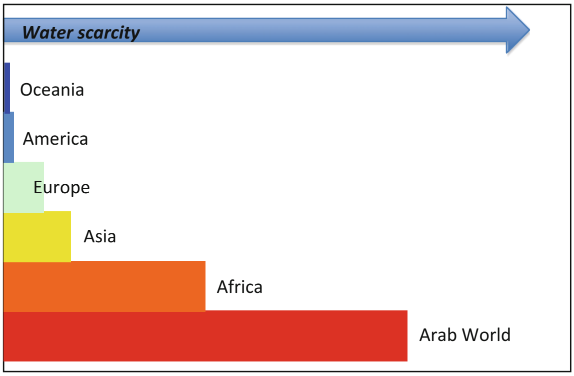

Fig. 1.1 The water scarcity by region II

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**.

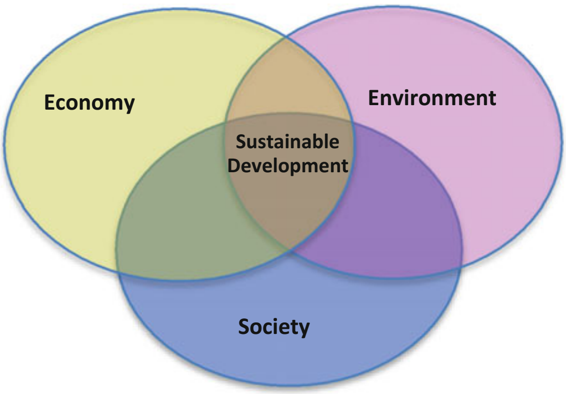

Fig. 1.2 Sustainability happens at the intersection of the three domains

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

[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.

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

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

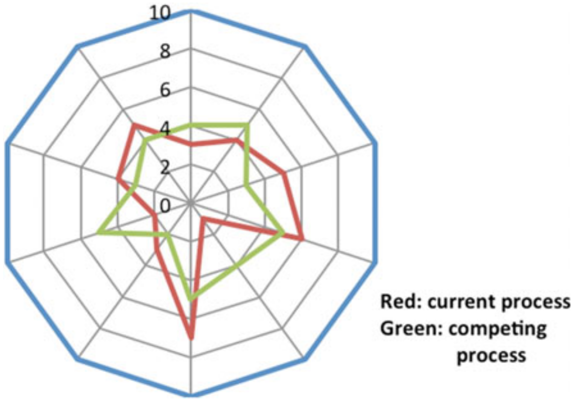

Fig. 1.3 Spider diagram for comparing indicator values

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 *j*th 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

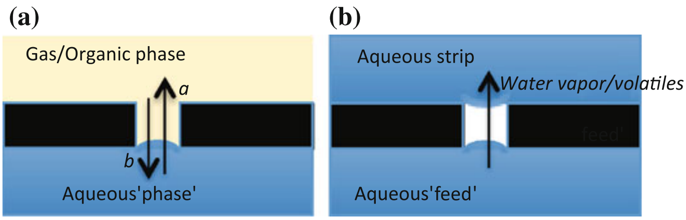

Fig. 1.4 Transfer of species between gas/organic and aqueous phases through a hydrophobic microporous membrane (**a**). Transport of water vapor and volatile species through the dry micropores of a hydrophobic membrane (**b**)

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

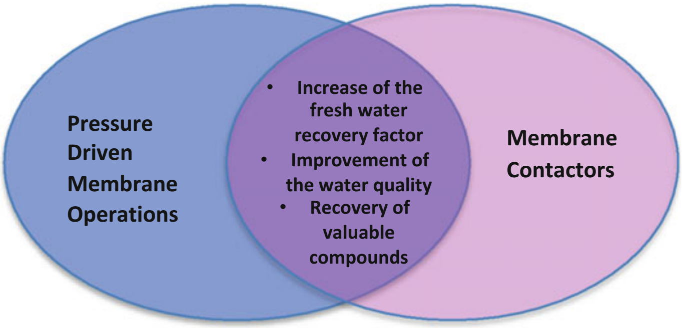

Fig. 1.5 The integration of different membrane operations as a means to improve the performance of the process

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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