Warsaw University of Technology

FACULTY OF BUILDING SERVICES, HYDRO AND ENVIRONMENTAL ENGINEERING

Water supply and division of Membrane technology

# Master's diploma thesis

in the field of study Chemical Engineering
and specialisation Industrial Security and Environmental

ANALYSIS OF DIFFERENT TREATMENTS MEMBRANE TECHNOLOGIES IN WATER INDUSTRY IN SPAIN

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## ABSTRACT

This thesis is going to explain in detail different membrane technologies for liquid solution such as Microfiltration, Ultrafiltration, Nanofiltration and Reverse Osmosis. Moreover, it is also going to present the common current applications, concretely, in water treatment in Spain, which they have been proved their removal efficiency and economic viability. This thesis pretends to prove the impact that membranes are having nowadays and how industrial facilities are increasingly close to the main environmental objective “zero discharge” due to implement membrane processes.

Key words: membranes, applications, water, Spain

## STRESZCZENIE

Teza ta szczegółowo wyjaśni różne technologie membranowe dla płynnych roztworów, takich jak mikrofiltracja, ultrafiltracja, nanofiltracja i odwrócona osmoza. Ponadto przedstawi również aktualne wspólne wnioski dotyczące oczyszczania wody w Hiszpanii, które zostały udowodnione w zakresie skuteczności usuwania i ekonomicznej opłacalności. Ta teza udowadnia, że udowadnia ogromny wpływ, jaki mają membrany na współczesność, oraz na to, że obiekty przemysłowe coraz bardziej zbliżają się do głównego celu środowiskowego, jakim jest "wyładowanie zerowe" dzięki wdrożeniu procesów membranowych.

Słowa kluczowe: membrany, aplikacje, woda, Hiszpania

# APPRETIATION

I would like to express my gratitude to all people that help to develop this project.

I start with my family because of their constant support and for making possible the opportunity of studying abroad and all the enriching experiences that I have lived here.

My supervisor in WUT (Warsaw University of Technology), Marek Apolinarski, for helping me whatever I need and his warm welcome received during the first days in Poland, the hardest ones.

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Professors of the Chemical and Nuclear Engineering Department of UPV for helping me in all enquires and doubts that I had during the elaboration, especially during the pursuit of companies' references.

# INDEX

# 1. INTRODUCTION

In the current industrial society, the use of membrane technology enables the mass production, the design processes, services or organizations, improving the capacity of innovation due to raise the value of these existences. That allows the companies to have more competitive advantages between other national and international companies.

Apart from economic benefits, enterprises have been forced to take another point into account. This is the environmental control which is regulated by different laws in order to reduce the impact of all the industry facilities that generate thousands of tons of different pollutants every day.

In fact, the main objective in this project is expressing the big impact that membrane technologies are having in our society and how many applications can have in it. The intention is to cover common applications which is typically used this technology, explaining in detail why is used this kind of technology for this specific application instead of other technology and how it works. At the beginning of each chapter, it will be an introduction comment explaining different points, such as, background, main issues or costs problems.

The development of membrane technology allows an approach to energy and resources saving, that also means an economical saving, and minimise waste. That is the reason that membranes are considered the most promising technology in environmental applications, making possible the reusing of resources of different output currents. This is a big step in the main environmental objective: zero discharge.

Membranes technology includes a big variety. In this project it is going to focus on those whose driving force is pressure-driven, treating liquid dilutions with organic membranes as separator element. In this field, it can be distinguished: Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO), which are commonly used to concentrate a pollutant as much as a viable point is reached.

Ultrafiltration and Reverse Osmosis are the main processes and they represent the limits in the range of particle size. From that, the rest of technologies have been developed in order to achieve specific separation applications. Since these processes, UF and RO, have proved their reliability and economics, all discussion of separation problems for fluid systems will almost inevitably lead to the question of whether the problem can be solved by membrane processes.

The decision as to whether or not a membrane process should be employed for a particular separation/concentration has to be based on an economic comparison with conventional processes such as distillation. In broad strokes, it must be evaluated the value of the resulted product versus the separation process cost which can be easily overcome by energy and other costs that separation requires.

All of these points will be treated in this project, starting with general points on membrane characteristics, transport theory and concentration polarization, gathering some common membrane technologies in water industry focus on Spain applications.

# 2. BACKGROUND

## 2.1. Definition of membrane

A membrane is a selective barrier that allows certain molecules or ions to pass through it by the mechanism of diffusion. Depending on the membrane selectivity, some components are able to come to the other side of the membrane while others are retained.

Simulating biological membranes which are essential to regulate the exchange of ions between cells inside the organisms, science has enabled the development of this technology and, nowadays, it is possible to create synthetic membranes as an alternative way for selective separations.

Membranes are normally accompanied by the word *semipermeable,* which means that membrane allows certain substances to pass through it but not others, especially allowing the passage of a solvent but not of certain solutes.

After that, it is common that membranes are confused with filters due to some similarities as the mechanism. Both are able to separate two components of one substance passing through it, but there are some different points to be taken into account:

- The direction of the substance is perpendicular in filters, and normally tangential in membranes. This operation mode makes that soiling is hugely decreased.
- Membranes are able to separate substances with a really small size due to substance interaction with membrane structure.
- The term filter is usually limited to structures that separate particulate suspension larger than 1-10 µm.

All of these points will be treated more in detail later.

As it would be commented, a membrane needs to interact with the substance to carry out the separation. In other words, the membrane must be sensitive to one or more molecular properties of the components. In order to achieve these properties in membranes, the manufacture process is the key.

Apart from that, the driving force is totally necessary for the separation between components. The difference of a physical-chemical magnitude between phases (gradient) produces a flux of components. Some examples of these gradients are pressure, concentration or temperature, and they are group together in a general magnitude known as chemical potential ($\mu$).

Particles tend to move from higher chemical potential to lower chemical potential. A component flux only take place adding the necessary energy for separation due to this process does not used to be spontaneous.

## 2.2. General aspects in membranes

In Figure 1 is represented schematically the performance in a membrane application which a feed current with two or more components mixed enter to a membrane module and separation between components takes place.

We can distinguish different currents:

- The *permeate current* is composed by the components which are passing through the membrane. This current used to have the value component in the mixture, although it is not necessary.
- The *rejection* or *concentrate current* is the feed current without permeate component.

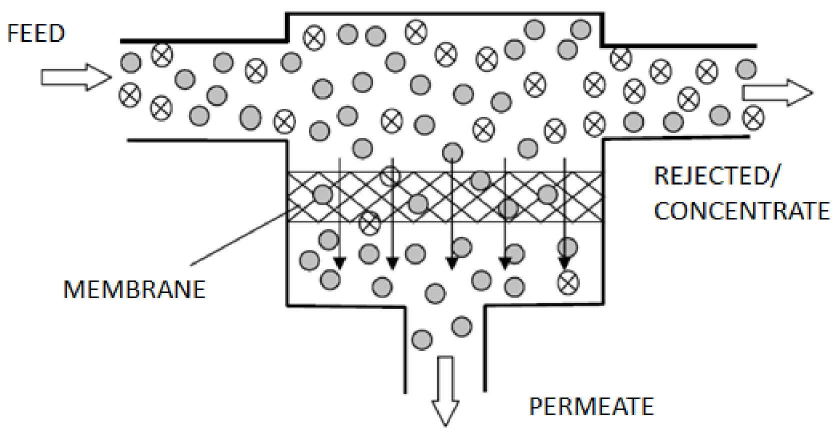


*Figure 1. Schematic draw of a membrane performance. [1]*

According to Figure 1, the performance of a semipermeable membrane is not a perfect process where removal efficiency is 100%. Feed current is composed by two components: dark particles and crossed line particles.

Membrane performances used to have one incoming current (feed) and two outgoing (permeate and concentrate). One of substances, the dark one, tends to permeate passing through the membrane and goes out the membrane module for permeate current. On the other hand, the other substance, the crossed one, is rejected by membrane and it goes out from membrane module as concentrate current.

In Figure 1, in both outgoing currents appear some particles of the other substance. That is the reason that removal efficiency is not perfect. Nevertheless, nowadays, specific technologies as nanofiltration and reverse osmosis are able to get values of removal efficiency of 99,3 %.

Membranes are classified depending on some generic parameters [1]:

- *Flux* (referring to permeate) is typically expressed as amount of dilution which passes through membrane surface. It is used to express the rate at which component permeates through the membrane, in other words, the amount of permeate per unit of the active surface of membrane area per unit time of exposition.
- *Selectivity* is referred to membrane ability to separate components of the feed in-put. About quantifying the membrane selectivity, there are different factors commonly used:

  - The *rejection rate (R)* about a specific component could be defined as the amount of particles of a component that has been removed from the feed current. It is calculated with the concentrations of feed and permeate steams and they always refer to the same component, that is the solute or the component to be removed, in this case component A.

$$R_A = \frac{C_{f,A} - C_{p,A}}{C_{f,A}}$$

  - The *selectivity factor between two components A and B*: is calculated with concentrations or molar fractions. The parameters *"y"* are referred to permeate concentrations and the parameters *"x"* are referred to feed concentrations. In this case, this factor takes into account both components of feed current.

$$\alpha_{\frac{A}{B}} = \frac{y_A/y_B}{x_A/x_B}$$

Thus, the most important membrane qualities are:

- High selectivity
- High permeability
- Mechanical stability
- Temperature stability
- Chemical resistance

In the top of the list, selectivity and permeability placed first. Both terms used to be related although they mean different things. Selectivity is referred to which component pass through membrane and permeability is referred to how much flux membrane is able to obtain.

## 2.3. Membrane classifications

A wide variety of membranes differ in chemical and physical composition and in the way of operation. Due to the multiple factors which can affect the efficiency of membranes and its permeability/selectivity such as, temperature or the pore size among others, characterisation of membranes has been necessary in order to prepare their classification.

In this chapter, it is going to study different classifications of membranes depending on different factors.

### *2.3.1. Structure of membrane*

The structure of membranes supposes to be one of the biggest influences of separation. The most common classifications are between porous and non-porous or dense.

Porous Membranes

As its own name says, this type of membrane contains pores in it. In fact, it is very similar in structure and function to a conventional filter.

This porous size determines the separation characteristics as the process takes place when particles have smaller size than the pore diameter. These are able to pass through the pores to the other side and particles which size are larger than the membrane pore, they are rejected. (Figure 2.1)

The bigger difference between the particle size which want to be removed and the other particles size in the feed current, the more selectivity would be able to reach by membrane. Therefore, separation of solutes by porous membranes is mainly in function of molecular size and pore size distribution [2].

This is the structure of membranes used in Microfiltration and Ultrafiltration, and it also is the base for their operating principle.

Non-porous, Dense Membranes

Non-porous membranes consist of a dense film instead of physic pores. These membranes are able to separate molecules with same size and it doesn't matter the state feed current (liquid or gaseous). These abilities are possible due to another separation mechanism which is called dissolution-diffusion. (Figure 2.4)

Then, component to be separated has to have chemical affinity with material which membrane has been made. In this case, firstly, the component will be dissolved in membrane and then it will be diffused because of the driving force (pressure, concentration or electrical potential gradient). Apart from that, the membrane structure must be *asymmetric* in order to this phenomenon takes place.

Mostly gas separation, pervaporation and reverse osmosis membranes use dense membranes to perform the separation.

The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material [3].

Another classification to be taken into account is if the structure is the same in all the membrane or change depending on the membrane distribution. That is called in membranes technology as symmetry.

Since 1960s, it started to mix different structures in the same membrane in order to improve the transport rate in separation processes for economic reasons. The transport rate of a species (in membrane) is inversely proportional to membrane thickness, so it must not be too thick to guarantee economic value.

This is so much important that fabrication an asymmetric membrane combining different structures until achieve good results is actually the major field of investigation inside membrane technologies.

<u>Asymmetric Membranes</u>

Asymmetric membranes consist of extremely thin surface layer supported on thicker and porous substructure. The layer is usually made by different polymers and its composition is extremely important due to separation takes place in it. This layer is known as “active layer”. The substructure gives mechanical characteristics as a support of the thin layer [3]. (Figure 2.2 and 2.3)

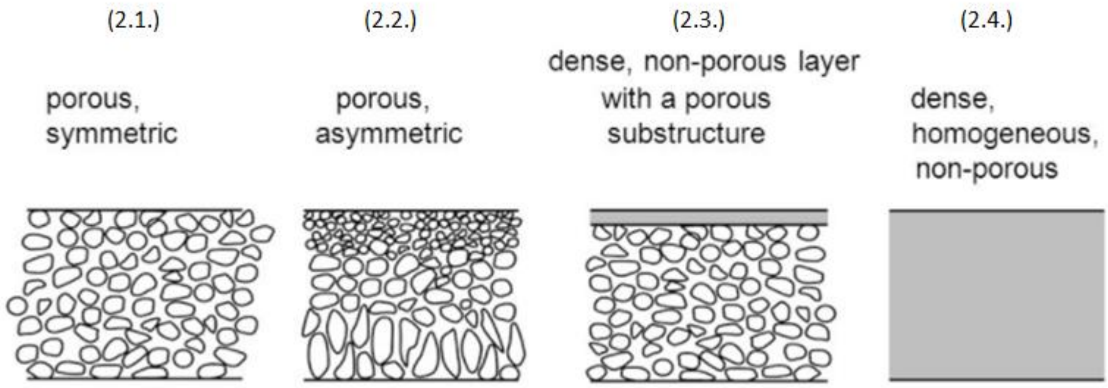


*Figure 2.Different types of structure in membranes. [3]*

### *2.3.2. Material*

Another classification of membranes is depending on the material which has been manufactured.

The selection of material is highly important as it determines most transport properties. In some cases, the influence will be lower, but in other it will be drastic. Apart from that, the material also influences preparative techniques which can be used and morphologies that can be achieved.

To sum up, material, morphology and manufacturing process will also affect the mechanical, thermal and chemical resistant properties [1].

<u>Organic membranes</u>

Organic membranes are based on polymeric materials and the variety of its structure is huge. The majority of membranes used commercially are polymeric based because of good results and economical values.

As it was commented, all the industrial processes that will be studied later use organic membrane equipment.

<u>Inorganic membranes</u>

Inorganic membranes are based on metallic or ceramic materials.

Ceramic membranes are being used because of solvent resistance and thermal stability. Metal membranes are useful with separation of gas mixture, for example, palladium membranes works well separating hydrogen in a mixture.

This type of membranes has more interest in recent years as they have different properties that organic membranes can't achieve.

### *2.3.3. Application*

This classification is too extensive to have only a sub-chapter, but it will be introduced in order to acquaint with some concepts that they will appear in the entire project.

This classification is based on the average pore diameter which results too difficult to measure directly and must often be inferred from the size of the molecules that permeate the membrane or other indirect techniques.

According to that, membranes can be organised into these groups, as it can be seen in Figure 3:

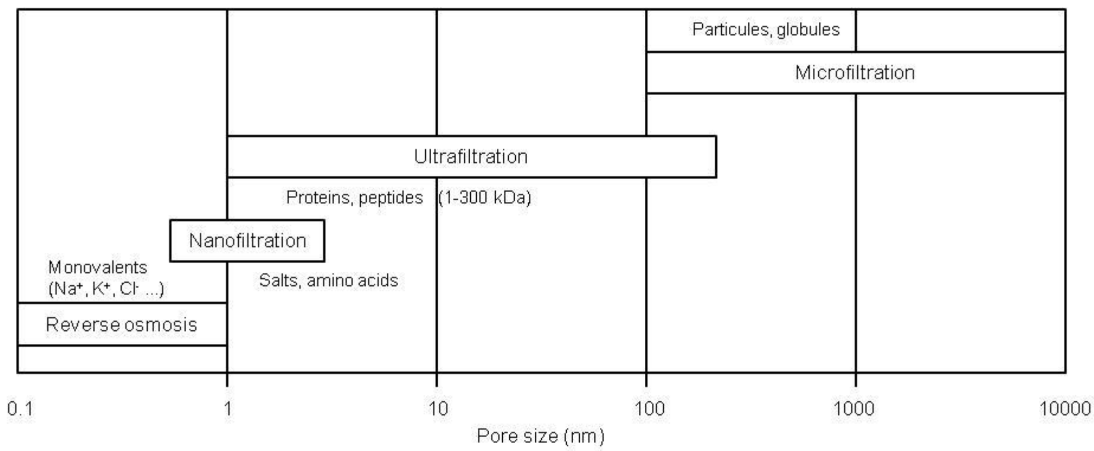


*Figure 3. Range of operation according to pore size of membrane in each technology. [7]*

- *Convectional filtration* is not consider as a membrane filtration (that is the reason that it is not contemplate in Figure 3), but it is useful to take into account as a reference due to it was the beginning of the investigation. Operation range: 1 - 150 micron.

- *Microfiltration*: the lower one. Very fine colloidal solid particles in the micrometre and sub-micrometre range; it can be removed from liquids and gases by microfiltration. It is able to separate most of pigments, bacteria, small dust particles, smoke, virus, colloid and proteins.
  Operation range: 0,05 - 3 microns.

- *Ultrafiltration*: This separation process is used in industry and research for purifying and concentrating macromolecular solutions. Microfiltration and Ultrafiltration are always compared together because both are based on size exclusion and particle capture system.
  Operation range: 0,004 – 0,2 microns. [5]

- *Nanofiltration*: This is quite recent technology. It is a liquid-phase separation which is able to remove dissolved solids, carried out by membranes with a relatively high pressure. Some applications are water purification, organic compounds or micro-pollutants removal.
  Operation rate: 0,001 – 0,01 microns.

- *Reverse Osmosis*: This technology can achieve the thinnest particle separation. Forcing the pass with special membranes with high pressure, it is possible to split sea water into brine and drinkable water, as it knows as desalination process, the most common one for RO.
  Operation rate: 0,1 – 1 nanometres.

## 2.4. Membrane transport theory

In this chapter it will be explained how membranes are able to select what substances pass through it and what substances are rejected in a mixture. The most important property of membranes is their ability to control the permeability of substances.

There are two principles, presents in Figure 4, depending on the technology used:

- *Pore-flow model*: permeate is transported by pressure-driven convective flow through the physical tiny pores. (4.1)
- *Solution-diffusion model*: permeate dissolve in the membrane structure and then diffuse through the membrane according to a concentration gradient (4.2).

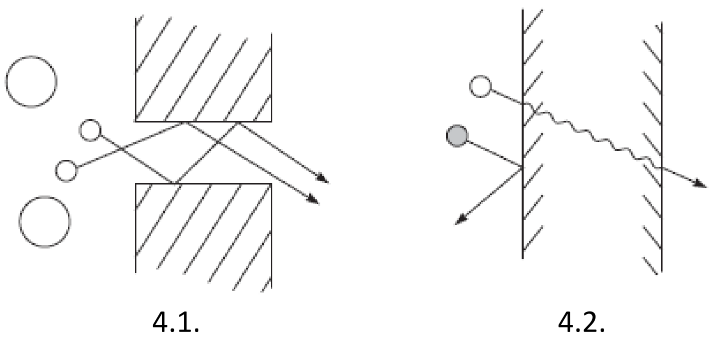


*Figure 4. Transport models for membranes: Pore-flow model (4.1) and Solution-Diffusion (4.2). [3]*

Transport between membrane takes place by the action of a driving force, which acts in the feed current side and whose magnitude is generally proportional of the permeation velocity. [8]

Pressure-driven convective flow, the basis of the pore-flow model, can be expressed the transport by the equation of Darcy's law as:

$$J_i = K' \cdot C_i \cdot \frac{dp}{dx}$$

Where $J_i$ is referred at rate of transfer or permeation flux ($m^3/m^2 \cdot d$) and $dp/dx$ is the pressure gradient through membrane with thickness $x$. $C_i$ is the concentration of the component $i$, and the constant $K'$ represents the nature of the medium.

On the other hand, if a concentration gradient is the reason which movement of the molecules is generated, it is diffusion process. The concentration gradient and the pressure as a driving force to impulse the pass through the membrane make possible the diffusion through membrane's structure.

Fick's law of diffusion can explain this transport technique by the equation:

$$J_i = -D_i \cdot \frac{dC_i}{dx}$$

Where $dC_i/dx$ is the concentration gradient varying over the membrane width. $D_i$ is called diffusion coefficient and is a measure of the mobility of the individual molecules. All the terms except dx are referred of a component *i*. [6]

If our process is a diffusion-controlled separation process, the most profitable thing to do for achieving useful fluxes across the membrane making the active layer as thin as possible and generating large concentration gradients based on the fact that the more difference of molecules are between the sides of membranes, the largest flux will be obtained.

The difference between pore-flow and solution-diffusion models lies in the relative size and permanence of the pores. [3]

- Membranes in which transport is best described by solution-diffusion model and Fick's law, the free volume elements (pores) in membrane are tiny space between of the polymeric molecules.
- Membranes in which transport is best described by pore-flow model and Darcy's law, the free volume elements (pores) are relatively large and fixed.

# 3. MEMBRANE TECHNOLOGIES

In this chapter it is going to explain the membrane technologies in detail in order to understand the individual issues of each technology and the different operation ways that they can have.

*Table 1. Pressure required and flux of permeate for each pressure-driving membrane process.*

| PROCESS | MF | UF | NF | RO |
|---|---|---|---|---|
| PRESSURE (bar) | 0,5 - 2 | 0,5 - 5 | 5 - 15 | 5 - 80 |
| FLUX ($L/m^2m$) | > 200 | 5 – 200 | 5 – 80 | 5 - 40 |

The relation between flux and pressure, visible in Table 1, proves the need of a driving force to guarantee the pass through the membrane for get a viable and "clean" permeate current. The less pore size the membrane technology used, the more pressure is necessary to be applied and the less permeate flux used to be obtained. This fact is quite obvious and it is clearly visible using the example of Reverse Osmosis and desalination process where drinking water are permeated leaving the tiny molecules of Sodium and Chlorine behind.

Based on the theoretical models purposed which are widely used to explain the transport of molecules through membranes, it can classify the difference technologies in some groups:

- Microfiltration and Ultrafiltration are explained by pore-flow transport model due to the wide range of pore size in the larger zone. It can be appreciated in Figure 3.
- Reverse osmosis contains a dense selective polymer layer with no visible pores (Figure 2.4). This process requires much smaller pores, as it directly means a permeate flux extremely lower in comparison with pore-flow. Transport in these membranes is best described by solution-diffusion model.
- Nanofiltration, the intermediate process between Ultrafiltration and Reverse Osmosis, was developed pretty recently. It covers some Reverse Osmosis applications without the necessity of using so high pressures.

All models try to find a relation between performance characteristics (selectivity and permeate flux) and operative conditions (solute concentration and operation pressure). Predicting the effect of varying operation variables to optimise the process is one of the most important objectives of characterising membrane technology processes.

*Table 2. Separation principles for different membrane technologies.*

| | **Compound size** | **Solubility and Diffusivity differences** | **Electrostatic effect** |
|---|---|---|---|
| **MF/UF** | **X** | | |
| **NF** | **X** | **X** | **X** |
| **RO** | | **X** | |

## 3.1. Microfiltration and Ultrafiltration

### *3.1.1. Introduction*

Microfiltration and Ultrafiltration are normally treated together due to their similarity of operated method, as it has been commented before. The principle is a physical separation. Both technologies are pressure-dependent processes and the separation completely depends on the pore size which must be smaller than the particles that want to be removed.

These technologies were the first ones to be developed due to their simplicity and similarity of conventional filtration. The beginning of Microfiltration can be dated on the nineteenth century with synthesis of nitrocellulose by Schoenbein in 1845, and continued in 1906 by Bechold, who was able to measure the pore size of his collodium membrane by a bubble point test. The first great application of Microfiltration happened in the Second World War, where there was an urgent need for an efficient method as a detection of serious pathogenic bacteria. [10]

According to manufacturing process, the best method which was firstly introduced in membrane technologies during 1960s by Loeb and Sourirajan was the Phase Inversion. Currently, it is still in use and it represents the base for the synthesis of most commercially viable membranes of Microfiltration and Ultrafiltration. [11]

Phase inversion process consists in the solidification of a thermodynamically stable liquid polymer solution. There are different ways to get this process though the Immersion Precipitation is the most widely-used membrane preparation method. This transformation from a liquid phase to solid phase takes place when a polymer solution is cast on a proper supporting layer and then submerged in coagulation bath containing non-solvent. The polymer must be soluble in solvent mixture. The precipitation is possible due to the solvent and non-solvent exchange.

This process is carry out in industrial scale, as it can be appreciated in Figure 5.

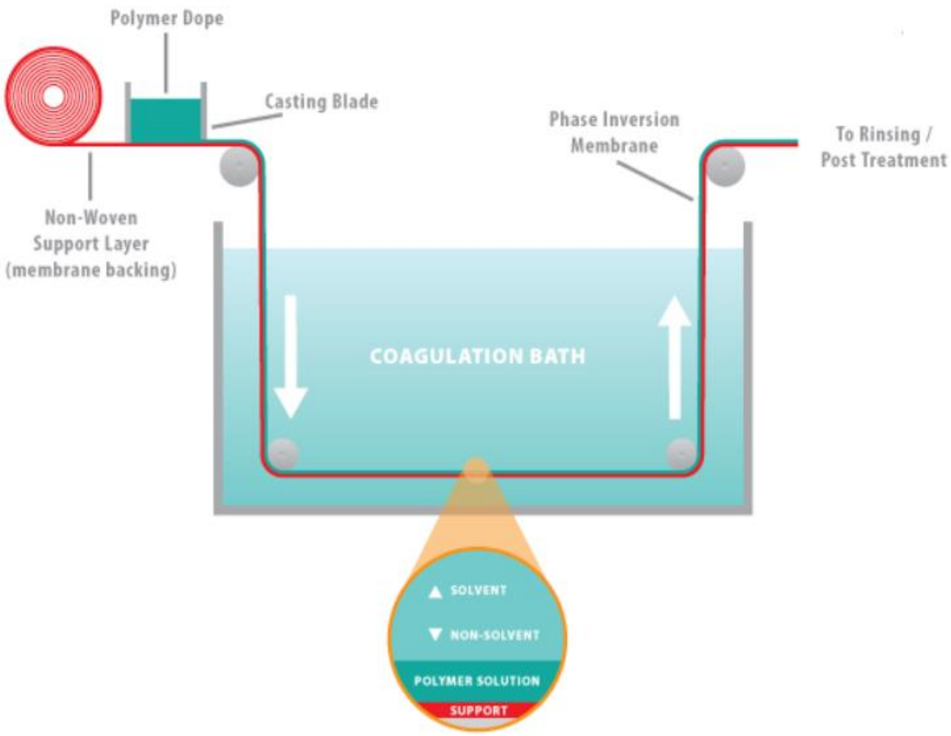


*Figure 5. Phase inversion technique in Industrial manufacturing membrane production. [12]*

### 3.1.2. Ultrafiltration

Ultrafiltration is a separation process based on size exclusion principle. UF can reject proteins, peptides, sugar, biomolecules, polymers, and colloidal particles.

One principle distinction of Ultrafiltration is its *molecular weight cutoff* (MWCO) which represents the ability of membrane and rejection takes place when the membrane presents a rejection equal or greater of 90%. Apart from that, membranes tend to retain smaller particles, providing them another deletion process. This fact happen because of a layer of solute which also contributes in a decreasing of permeate flux. [10]. This MWCO varies with chemical characteristics of feed current and membrane configuration.

In comparison to Microfiltration, Ultrafiltration needs more pressure to guarantee the pass through the membrane, as it is visible in Table 1. The osmotic pressure is increased in UF becoming significant.

The *osmotic pressure* is defined as the minimum pressure needed to be applied to a solution to avoid the pass through a semipermeable membrane from the less concentrated side to the more concentrated. This process takes place naturally due to a chemical potential difference, generated by the solute concentration gradient.

Dutrochet was who named first in 1828 the *osmosis* as the diffusion of water through a semi-permeable membrane to the lower concentration side (higher chemical potential) to the higher concentration side (lower chemical potential) until the chemical equilibrium is reached.

The osmotic pressure, generate initially as the concentration difference, is counteracted with a hydrostatic pressure which tend to pass the solvent of the more concentrated side through the less one, appearing a difference of height *Δh*, present in Figure 7. [14]

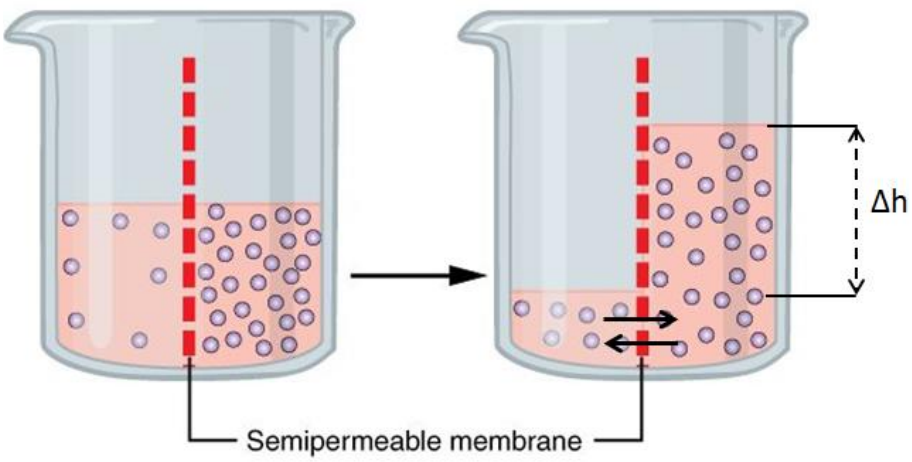


*Figure 6. Osmosis process between a more concentrated solution (hypertonic) and a less concentrated solution (hypotonic) separated by a semipermeable membrane. [15]*

In the end, the hydrostatic and osmotic pressure are equalised and the flux through the membrane stop. The difference of concentration still belongs but the hydrostatic pressure prevent from equalling concentration in both sides.

Coming back to Ultrafiltration, the influence of osmotic pressure is higher and the permeate flow is strictly studied although it is limited by polarization by concentration fouling and the own resistance of the membrane.

Larger particles than the membrane pores are not able to pass and they tend to accumulate in the proximities of one side of the membrane, creating another concentration gradient between the proximities of membranes ($C_G$) and the feed dissolution ($C_B$), according to Figure 8. Eventually, particles concentration in the proximities are so high that a gel is formed, creating a gel layer. This process is called *polarization by concentration*. [16]

Initially, gel layer can be a benefit for the separation process as it helps to retain particles. Nevertheless, in some point, the thickness of this layer will be so high that the permeate flux will have a constant value and it won't change although the pressure increase.

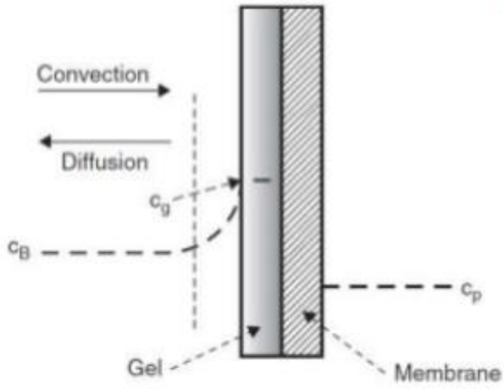


*Figure 7. Polarization by concentration phenomenon in the proximities of a UF membrane. [16]*

This phenomenon can be solved operating with high speed and using turbulence promoters (metallic structure with small squares that improve turbulence in the membrane proximities) in order to avoid the accumulation process.

To sum up, Ultrafiltration presents two general limitation that are directly influence the process:

- *Fouling resistance* is the group of resistance of adsorption, formation of layer cake and blocking pores.
- *Resistance of membrane* depends on geometrical factors, such as, pore size distribution, thickness and membrane hydrophobicity.

Apart from, obviously, the characteristic of the feed current are also taking into account during the design operation of membranes, specially the viscosity.

To explain the transport mechanism that takes place in Microfiltration and Ultrafiltration membranes, can be used physical models in order to simulate these processes in advance. [17] These one are the most common ones:

- Resistances in series model.
- Concentration by polarization.
- Transport of mass model.
- Nodular type model (Kozeny-Karman)
- Capillary type model (Hagen-Poiseuille)

### 3.1.3. Microfiltration

Microfiltration process can be understood as a technique of separation, able to remove particles with sizes of micrometres scale such as bacteria, yeast cells, colloids and suspended particles. These particles are relatively big between 0,05 – 5 µm and operating between 0,5 – 3 bar.

In this process, the membrane pore size is bigger than Ultrafiltration or Reverse Osmosis, consequently the microfiltration process has bigger permeated fluxes, as shown on Table 1. The driving force makes the fluid and the smaller diameter particles go through the membrane and are collected as permeated. Instead, the bigger particles are removed as concentrate. [10]

Microfiltration can be done on two different ways (Figure 6):

- *Dead-end configuration:* the feed flux goes to the membrane surface perpendicularly. The particles tend to accumulate along the filtration process, concretely along the active area of membrane surface, forming a “cake layer”, which produces a drastic decreasing of permeate flux. This method requires stopping the process and removing the solute layer or replacing the membrane.

- *Crossflow configuration:* the feed flux goes to the membrane surface in parallel. This configuration born as a need of a more viable method due to the inability to dead-end configuration treating mixtures with high level in solute. This configuration produces a high decrease of cake layer. For all their advantages, this configuration is also used in Ultrafiltration, achieving a stable flow eventually and then, decreasing slowly.

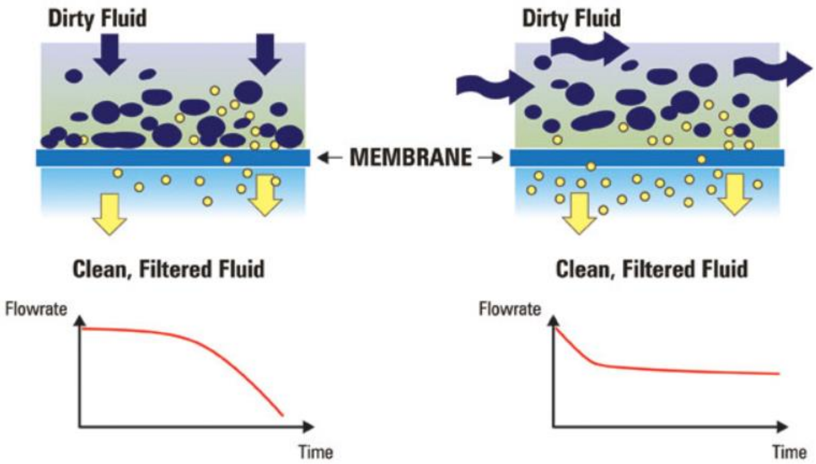


*Figure 8. Visual representation and permeate flux evolution with time of filtration in dead-end configuration (left) and crossflow configuration (right). [13]*

## 3.2. Nanofiltration

Nanofiltration is a relatively recent membrane technology which its origin is dated in 1970s and applied industrially in 1980s. This technology born when Reverse Osmosis membrane were able to operate with a reasonable water flow with a relatively low pressure. A lower operating pressure directly means a reduction in energy cost. [10] The NF process is essentially a liquid phase because it separates a range of inorganic and organic substances from solution in a liquid mainly water. [27]

Until NF was defined, manufactures refer to *intermediate membranes* between UF and RO as a *lower-pressure RO* or *tight UF* membranes. In the end, in the years 80, the definition of NF was definitely defined to membranes which reach some requisites [19]:

- Pore diameters of less than 2 nanometres.
- Significant passage of monovalent ions.
- Larger divalent ion rejection than monovalent.
- MWCO for neutral species in the range of 150 – 2000.

NF membranes operate on porous and non-porous membrane interface. That structure made that NF shares the transport mechanism of UF and RO and, in broad strokes, it also shares the advantage of UF for using less pressures to perform the separation and the advantage of RO for getting more concentrated current in rejected line. NF separation principle combines the transport mechanism of the other membrane technologies, prevailing the mechanism of diffusion and particle size limitation.

As all asymmetric membranes with a dense active layer, the main working principle is the combination of hydrophilic and hydrophobic properties of the different materials of the membranes. The hydrophilic active layer, where the separation takes place, allows the solvent interact with it and pass through membrane rejecting the solute.

Apart from that, NF membranes present electrical characteristics. The NF membrane contains ionisable polymer groups, like carboxylic and sulfonic acid groups, resulting slightly in charged at neutral pH in contact with the aqueous solution due to the dissociation of functional groups or surface adsorption of solute. This electrostatic characteristic is specifically for NF and it plays an important role providing it an extra reject for negative ions. This electrostatic interaction was described as Donnan exclusion effect. [20]

It is visible in Figure 9 the hydrophilic properties of the active layer polymeric material which allow the water to pass through the membrane and the electrostatic interaction between the ions in feed and membrane.

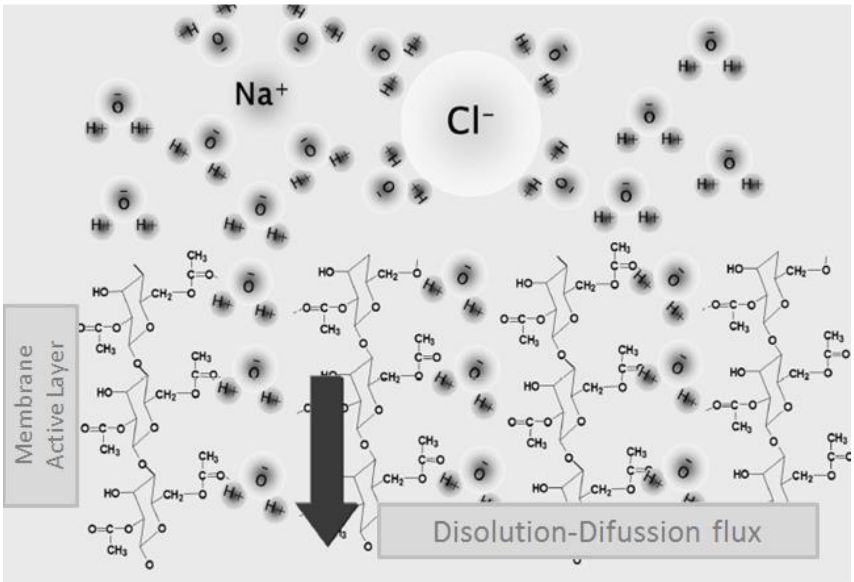


*Figure 9. Desalination process of brackish water with NF membrane technology. [17]*

In order to predict the behaviour of membranes, phenomenological models are well recognised although they do not consider the transport mechanism. This type of models relates flux and driving force which is multiply for a phenomenological coefficient. For NF, the best know model is the Kedem-Spiegler one. For some membranes, Dissolution-Diffusion model gets to predict better explanation due to the asymmetric structure, although it is more specific for Reverse Osmosis. Finally, the Fixed Charged model is also a good one due to is specifically for this technology.

As with any other membrane process, NF is susceptible to fouling and it must be designed to minimise it with proper pre-treatment, right membrane material and proper cross-flow velocities to scour the membrane surface clear and using rotating or vibrating membrane holders. [27]

Industrial applications of NF are common in food and dairy sector, chemical processing, in the pulp and paper industry, in textiles and process of waste water, specially removing natural organic matter, tastes and colors. It is also used in desalination, but only for brackish water. [27] Some of the most common NF applications are: desalinization of lacteous products, sugars concentration, soluble pigments and tints purification, water softening, pesticides removal from ground waters, heavy metal removal from residual water, nitrates removal, residual water reusing in laundry. [17] Similar to RO membranes, NF membranes are really useful separating inorganic salts and small organic molecules.

### 3.3. Reverse Osmosis

Osmosis process was discovered in the XVIII century. Fick and Graham made first methodological observations of membrane permeation and later the osmotic pressure measurements were performed by Traube and Pfeffer. In 1887, Van't Hoff got to explain the behaviour of ideal solutions diluted. [10]

The osmotic pressure was the pressure which must apply to a solution to stop the dissolvent flux through a semipermeable membrane. When osmosis process takes place, the dissolvent pass through membrane from the less concentrated side to the more concentrated one and it is formed a pressure difference in both sides of membrane which name as the osmotic pressure, as it was commented in Figure 7.

Reverse Osmosis, as its own named indicates, consists in applying a pressure greater than the osmotic pressure in order to force the dissolvent pass through the asymmetric membrane. It was also commented that NF and RO used membranes with two different structures in order to achieve the rejection of tiny particles presents in feed. Visible in Figure 10. [21]

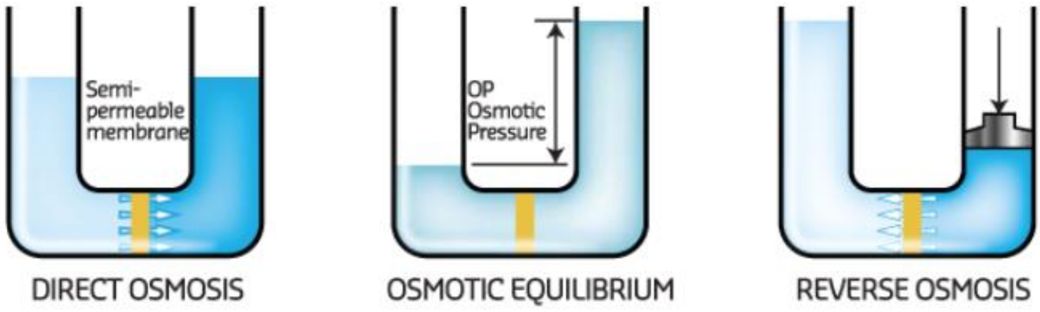


*Figure 10. Schematic draw of Direct and Reverse Osmosis. [22]*

These membranes have a dense active layer where separation takes place and a porous support just behind which provides mechanical resistance and an improvement of permeate flux, as it shown in **Figure 11**. Polymeric chains of dense layer have intermolecular spaces, as it is shown in **Figure 9**, and present affinity with the feed component, creating weak bonds with water molecules and not with sodium chloride.

As it was commented, RO membranes behavior can be predicted quite accurately with dissolution-diffusion model which affirm that firstly water is dissolved in the dense structure due to its hydrophilic affinity and then it is diffused through porous layer with the help of external pressure. [23]

It is really important to control the membrane structure and manufacture membranes technically in order to improve the membrane selectivity which depends essentially on the chemical nature.

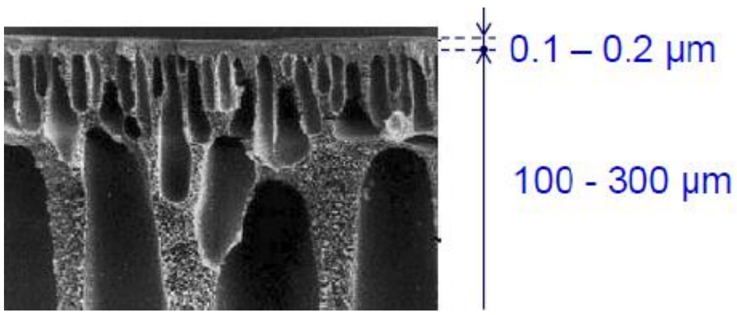


*Figure 11. Asymmetric membrane with each structure length. [11]*

Reverse Osmosis is currently the most efficient large-scale desalination process. It is also used for water purification removing ions and very low molecular mass particles. This technology is able to achieve almost perfect rejection. In 1959, Reid and Breton already got to remove salt from water using a cellulose acetate membrane with a 99%

salt rejection results. [10] But it was not until 1965, when Loeb and Sourirajan discovered the big benefits of using an asymmetric membrane, specially the improvement of permeate flux. [24]

RO has overcome other desalination process like electro dialysis, ion exchange or traditional thermic process like Evaporation due to an important improvement in energy consumption to produce big amounts of drinking water cubic meters.

Different studies have confirmed the average energy to overtake the osmotic pressure of sea water. The minimum needed energy is between 0,78 - 0,83 MWh/$m^3$ which is applied by pressure. Unfortunately, RO is not a perfect process and it needs more energy than the minimum due to several reasons [23]:

- Feed flux is larger than permeate.
- The sea water osmotic pressure inside the reverse osmosis module is bigger than the sea water one.
- Friction loss in pipes.
- The pumps do not transform all the energy to impulse the water.

As it was commented above, RO used to performance inside modules for several reasons [24]:

- Avoiding leaks between feed and permeate.
- Assure the maximum membrane area per volume with a compact structure.
- Assure the minimum feed in order to limit dirtying in membrane surface.

There are different RO modules types allow in the market:  tubular, plates, hollow fiber and spiral, although for Reverse Osmosis systems for desalination of seawater, spiral modules are used most often due to some advantages such as cost, space required and design flexibility. [25]

Spiral modules consist of an asymmetric membrane rolled as a spiral, taking the active layer towards the exterior with the purpose of feed water enters the module parallel to this making permeate water towards the interior part of the module and leave the for the opposite part of feed current. It is more visible explained in Figure 12.

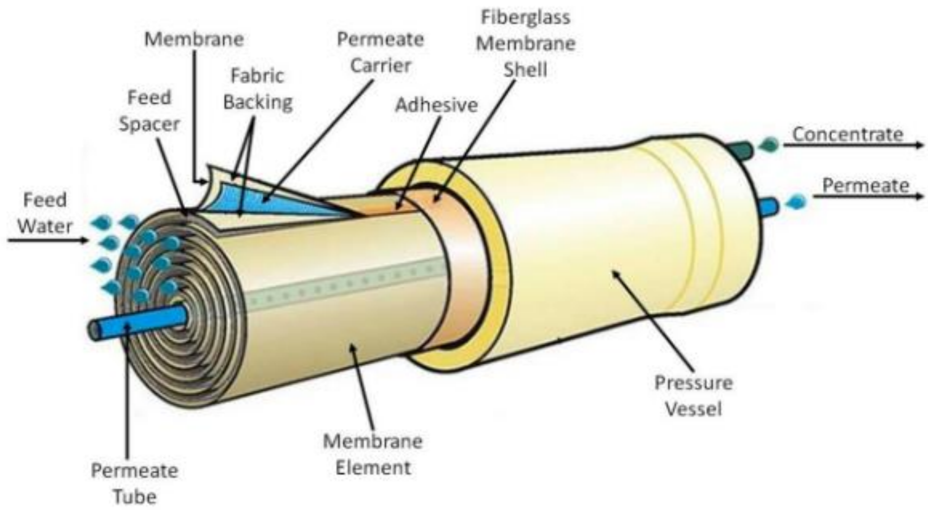


*Figure 12. Schematic draw of a RO spiral module.* [26]

In the image, it is visible the different parts of a module, the feed entrance entry the module perpendicularly. Between membrane layer and membrane layer, there is a *permeate carrier* which favours the entrance of water and improves the turbulence for avoiding fouling. The water pass through all different layer retaining all particles that water could contain until arrives the central tube where permeate leaves. Contrary, the concentrate current (brine) leaves the membrane for the opposite side of feed current and it is accumulated for receiving a pre-treatment before of being returned to the sea.

# 4. SPECIFIC INDUSTRIAL APPLICATIONS OF MEMBRANES TECHNOLOGY FOR WATER TREATMENTS IN SPAIN

## 4.1. Ultrafiltration

As an example of the technology of Ultrafiltration in industry scale, it has been selected the "Benidorm Sewage Treatment Plant", where UF represents the pre-treatment for assure the proper feed for another delicate and sensitive process, in this case a Reverse Osmosis, in the third treatment.

### *4.1.1. Introduction*

Sewage Water is considered to all water whose quality has been affected negatively. Its origin can be domestic, urban, industrial or mixed with others. This kind of water must be taken into account as it supposes a risk for the public health and environment and it may affect a big amount of population easily if it is not treated.

Nowadays, it has its own standardised processed which combine different processes depending on the water characteristics, the amount of water and the final water needs according to the discharged legislation.

The decontamination of this kind of water in populated places takes place in Sewage Treatment Plants where their main objective is to remove all chemical and biological pollution of water which can be harmful for human, flora and fauna.

This type of plants used to have these steps [27]:

- *Pre-tratment*: In this phase takes place different operations, such as, controlling a constant flow with by regulation systems and removing big solids easily collected by bar screens and flats. This process eases pumps and other mechanical systems maintenance.
- *Primary treatment*: This phase is dedicated for sedimentation and it is composed by large tanks used to settle sludge while grease and oils rise or drop where is removed. In this step it is common to add chemicals like coagulants and flocculants to ease the separation of small suspension solids and colloids. This process used to last between one and two hours and is able to remove between 60 and 70% of suspension solids.
- *Secondary treatment*: This phase is designed to degrade the organic matter of water which is derived from human waste, food and detergents. This process is taken place by a biological oxidation followed by sedimentation. It is a controlled natural process which microorganisms, present in waste water, feed by solids and colloids as food, producing carbon dioxide and water, originating biomass that is collected at the end of the decanter. First, water pass through

an aerobic biological reactor, and then, the decanter where biomass (bacteria) must be treated.

- *Tertiary treatment*: In this phase, the main objective is improve the effluent quality before be discharged to the environment. It is focused on remove some specific pollutants like phosphates, really commonly by detergents avoiding the eutrophication.

The tertiary treatment is not always present in Sewage Treatment Plants despite it guarantees much better purification, but sometimes it is not necessary to be included to discharged the water. It depends totally by the characteristics of water.

### 4.1.2. Benidorm Sewage Treatment Plant

Benidorm, situated in the Valencian Community region, was one of the pioneers in sewage treatments and its plant was built in 1984. Benidorm was also important to be one of the first Spanish plants reusing its treated water in irrigation. This supposed a big change, due to the abundant available clean water, especially for zones like Benidorm with constantly drought risk.

During first years working, engineers realised that there was a big increase during the sunny months and the plant were not able to treat enough water. Apart from that, the feed water was not constant and almost all the demand was during the day hours. These problems were solved by the building of a pool to regulate the feed water more easily (1995) and the extension of the depuration capacity from 40.000 to 62.000 $m^3/d$ (2006). [28]

In spite of the remodelling, the plant continues having the same capacity problems due to a geographic and tourism growth. For cold months, the water required was minor and its quality was better. Unlike, for summer months, the irrigation needs increased considerably, although its quality decreased, caused by it was mixed with no treated water.

Apart from that, Benidorm started to suffer another problem, the increase of salinization. Its causes are not well known: discharges of water softeners from tourist companies, infiltration of sea water, dumping of highly salinized water… Salinity got that conductivity achieved average values of 2.400 µS/cm, when the recommendable value was 2.000 µS/cm. On December of 2010, the conductivity was 3.000 µS/cm and the water started to be dangerous to irrigation. In that moment, the installation of a tertiary treatment project was taken seriously into account.

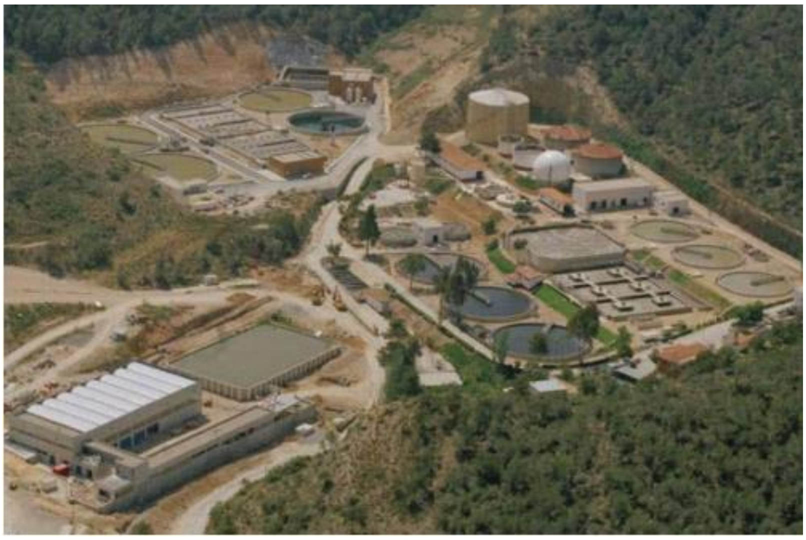

*Figure 13. Benidorm Sewage Treatment Plant.* [28]

### *4.1.3. Ultrafiltration in Tertiary Treatment*

The tertiary treatment was built in 2006; it is close to the pool of irrigation water due to this is the only water which really needs the treatment. The rest of water achieved the legislation and could be discharged directly after the primary and secondary treatments.

The tertiary treatment for this particular plant consisted of a desalination process in order to reduce concentrations, such as 670 mg/L of sodium chloride and 450 mg/L of other salts. As all membranes processes, especially those that use asymmetric membranes must have a pre-treatment to remove large particles, so that in other case, the NF/RO membranes would be useless.

The desalination plant has a capacity of 33.000 $m^3$/d, being the design Sewage Treatment Plant capacity of 62.320$m^3$/d. This tertiary treatment consists of the ultrafiltration and the reverse osmosis membranes at the first moment (2006), but it was extended adding a homogenization tank (8.500 $m^3$), a coagulation/flocculation and UV disinfection processes (2010). [29]

The Ultrafiltration system consists of six parallel pipes, where each one contains a six submersible hollow fibre and other supplement membranes. In total, it is composed by 57 *Zenon UF Zeeman Weed Model 1000 V3* modules. The specific operation flux is 16 – 21 $L/m^{-2} \cdot h^{-1}$ with a 90% of conversion.

This treatment is quite versatile and can combine different processes according to the water destination [29]:

- First alternative: Homogenization + Coagulation ($FeCl_3$)/Flocculation + Filtration + UV Disinfection + Mixed with ultrafiltrated water
- Second alternative: Homogenization + Coagulation ($FeCl_3$)/Flocculation + Filtration + Ultrafiltration + Mixed with filtered water
- Third alternative: UF water→ Cartridge filters + Reverse Osmosis

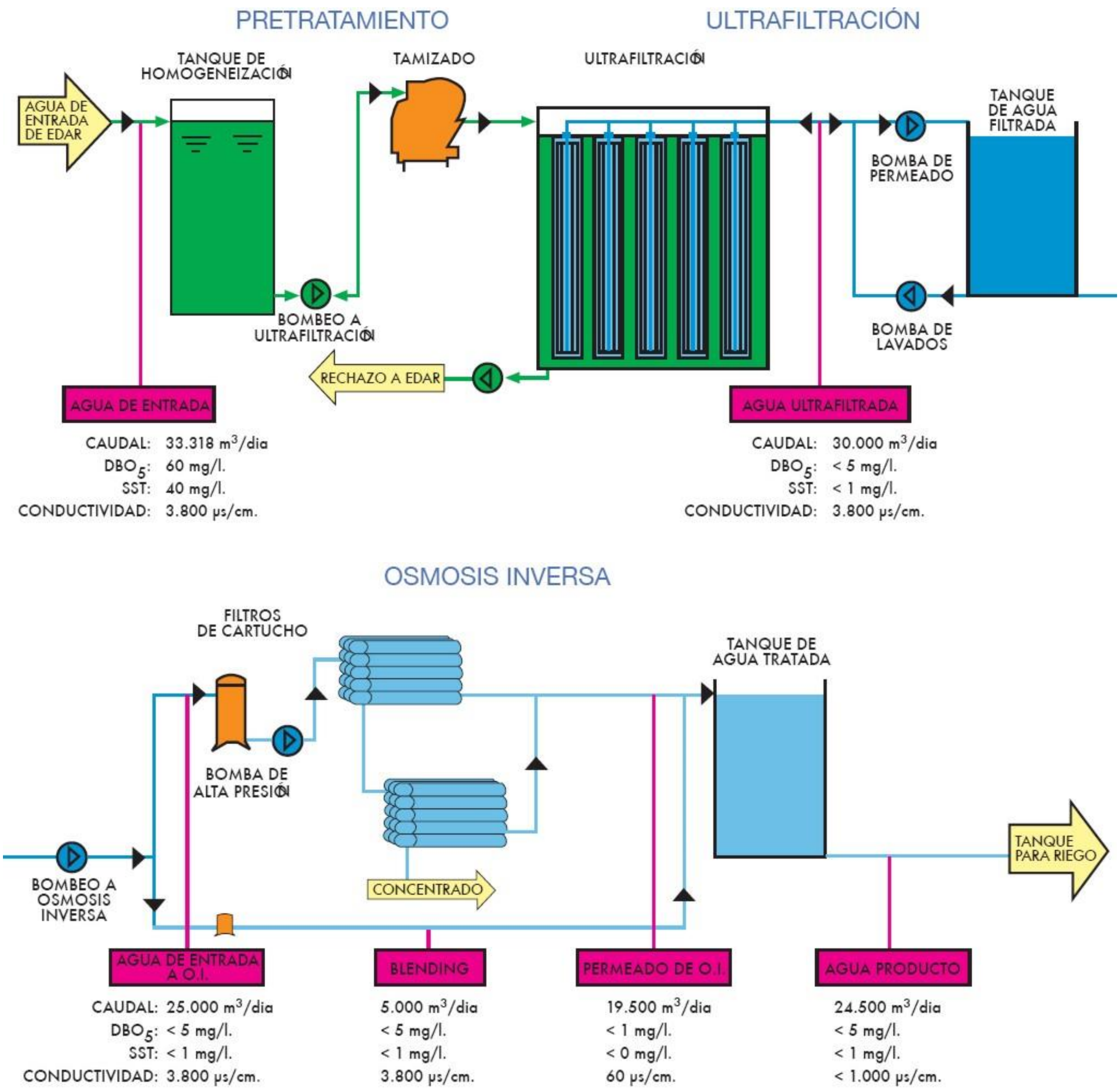


*Figure 14. Flow chart of Tertiary Treatment of Benidorm Sewage Treatment Plant. [28]*

According to 2015 data, the Benidorm Plant got to regenerate 5.705.116 $m^3$ of depurated water: 2.062.233 $m^3$ (first alternative), 2.067.331 $m^3$ (second alternative) and 1.575.552 $m^3$ (third alternative), being the Ultrafiltration process the most productive alternative.

*Table 3. Water quality in different points of the Benidorm Sewage Treatment Plant in 2015, where SS is the Suspension Solids concentration, $DBO_5$ is the Biological Oxygen Demand in 5 days and DQO is the chemical oxygen demand. [29]*

| | | Tertiary treatment exit | | |
|---|---|---|---|---|
| Parameter | Secondary treatment exit | First alternative | Second alternative | Third alternative |
| pH | 7,4 | 7,4 | 7,4 | 6,5 |
| SS (mg/L) | 24 | 9 | <1 | <1 |
| $DBO_5$ (mg/L) | 23 | 14 | 6 | 3 |
| DQO (mg/L) | 66 | 50 | 21 | 5 |

As it is observed in Table 3, the regenerated water quality in all the alternatives is good, especially for the third option using Reverse Osmosis. Ultrafiltration alternative is a good method to operate, and it perfectly achieve the quality requires of RD 1620/2007.

This tertiary treatment has supposed to reuse waste water in irrigation in a secure way after the increase of salinity between 1998 and 2005. Benidorm Sewage Treatment Plan has received continuous improvements and extension of its capacity according to the demand growth.

Additional information:

The Sewage Treatment Plant belongs to a Benidorm Local Government. External companies are responsible to make use of the plant.

- "*Aquambient Servicios para el sectos del Agua S.A.U.*" works with the plant.
- "*UTE SAV-DAM-DRACE Medio Ambiente S.A. UTE III Benidorm*" Works with the tertiary treatment.

## 4.2. Microfiltration

Microfiltration is the lowest capacity of the separation processes in membrane industry. For this reason, it used to be a phase accompanied with other processes, in other words, as equal as Ultrafiltration, Microfiltration, most of the times, represents a pre-treatment for another process.

Due to confidential issues, the design of a practical industrial-scale MF process has not found. However, there are several experiments with this technology treating derivatives in food and drinks industry. Next, it is going to present an experiment where it is used the obive cheese whey in order to valorise this by-product which affects really negatively the water.

### *4.2.1. Introduction*

Milk serum (whey) is a sub-product originated during the cheese elaboration when it is separated from the curd. This product has reveal appearance and yellowish colour. It contains 6% of solids (70% lactose).

This derivate represents a high pollutant power due to the high organic material content. Actually, the problem is the lactose which can act as a substrate in the microbial fermentation. Whey is catalogued as highly pollutant as it generates 35kg of Biological Oxygen Demand (BOD) and 68kg of Chemical Oxygen Demand (COD). [30] Moreover, this derivate is generate in big amount, approximately, 9 litres of whey for each kilogram of cheese produce.  That supposes a big risk of water and environment pollution.

Until relatively recently, whey was discharged without any treatment but, nowadays, it is transformed in high added value products. Legal requirements forced cheese industry companies to treat their effluents, supposing a great economical inversion due to whey represents between 80 – 90 % of produced milk. [31]

In Spain, the production of cheese is stabilized in 300.000 tons, and it can be estimated 2.700 million of whey litres annually. Although there are some big cheese producer companies, generally, the cheese industry is distributed in small and medium installations, hindering the proper whey treatment for lack of the proper technology.

Initially, whey was transform in powdered whey by evaporation and drying, obtaining a protein enriched fodder for animals, and lactose was produce by evaporation and crystallization. Currently, looking for more sophisticated and environmental respectful treatments, it started to study the possibility of isolating the protein and nutrient rich parts of milk serum with membranes.

### *4.2.2. Microfiltration pilot plant*

As it was commented, in this chapter it is going to present an application of membrane technology in a pilot plant in order to treat whey and looking for some economic benefit in it. This project was requested by "Serra de Estrela".

Before presenting the pilot plant, the feed samples must be described. The samples of whey were provided by "Serra de Estrela". Samples were refrigerated immediately after the cheese production and they were stored in metallic recipients. During the transport, it did not last more than three hours until the pilot-plant reception.

Until the extraction of the nutrient and protein from whey, there are some "purification" processes in order to remove the residual lipid-containing material to the globular proteins which constitute the majority of whey proteins [32], apart from guaranteeing a proper concentration process, where it actually takes place in Ultrafiltration process. Then, Microfiltration is a pre-treatment in this process, as it has been commented before, and it is exactly what profitable it can be.

The clarification step is composed by a thermocalcium precipitation and a Microfiltration process. The clarification of separated refrigerated cheese whey used in this experiment is follow the experiment by Fauquant (1985):

Firstly, the thermocalcium precipitation which requires: a Calcium adjustment until getting 1,2 g/L using $CaCl_2$, a pH fit 7,5 using NaOH and heat up quickly until 50$^{o}$C and cold down until 4 – 6 $^{o}$C until the next day. And secondly, the Microfiltration of the result of previous precipitation which took place in a pilot plant with these characteristics:

- Porous hollow fiver membrane: CFP-2-E-35 A model, pore size 0,2 µm (intern diameter 1mm and 0,8 $m^2$ area) and CFP-6-E-35 A model, pore size 0,65 µm (intern diameter 0,75 mm and 1 $m^2$ area), supplied by A/G Technology Corporation.
- Pressure: 1,6 – 1,8 bar.
- Recirculation flux: 2.000 L/h.
- Volumetric Concentration Factor (VCF): 5 (final retain volume is 20% of initial volume).
- Temperature: 8 – 10 $^{o}$C.

After that, it is presented the pilot plant, Figure 13, in where it will be the same for Microfiltration and Ultrafiltration, changing the module.

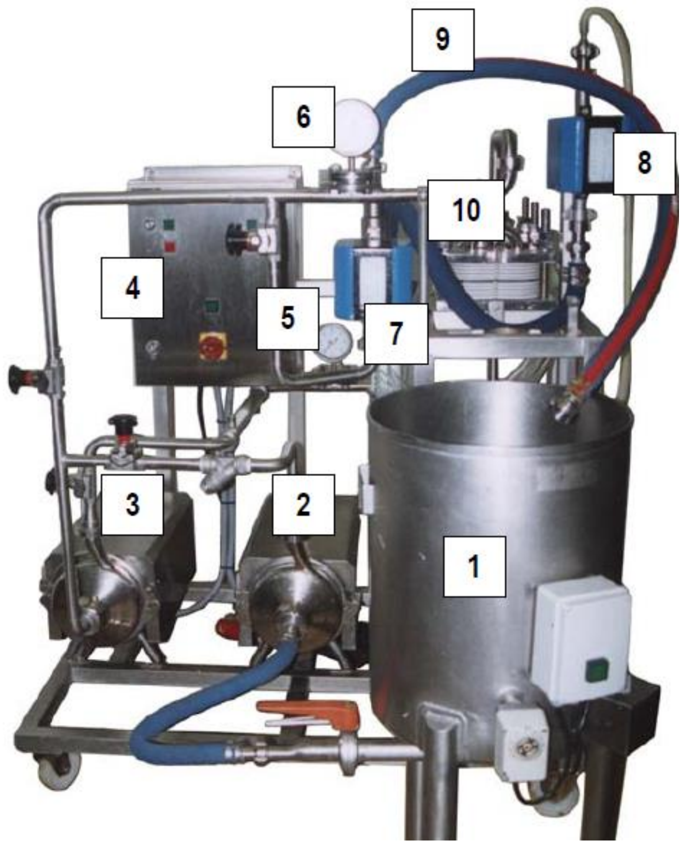


*Figure 15. Membrane pilot-plant: (1) Feed tank, 50L, (2) Feed centrifugal pump, (3) Recirculation centrifugal pump, (4) Control panel, (5) Manometer, module entrance, (6) Manometer, module exit, (7) feed flowmeter, (8) permeate flowmeter, (9) thermometer, (10) Membrane exchangeable module type Pleiade UFP 10 BIO.*

After clarification, the permeate of previous Microfiltration is ready to be treated by Ultrafiltration-Diafiltration (UF/DF) where the high protein concentrates appears.

The first result is easily notable that clarified whey showed superior UF fluxes with quite better conditions than without this process. Between the tested membranes, 0,20 µm and 0,65 µm, 0,2 µm membrane has proved to be more profitable. Considering the relative permeation flux, calculated as the division between the average of relative permeation fluxes of clarified and non-clarified products, the 0,2 µm membranes has improved 3,2 times, and, for 0,65 µm, the improvements were 1,6 times.

Nevertheless, the 0,2 µm is pretty more time-consuming than the 0,65 µm due to be the pore size three times lower. In fact, 0,65 µm membrane showed an average permeation rate of 31,1 ± 5 $L/m^2 \cdot h$ and, for 0,2 µm, 19,1 ± 7 $L/m^2 \cdot h$. Really issue to take into account when it becomes an industrial process.

The protein obtained after diafiltration are good enough for protein-rich concentrate matter. MF treatments have been able to remove until 63% of the fat detected in skimmed products, easing considerately UF/DF work making better conditions as a feed in this process and increasing its fluxes.

Regardless, CFP-6-E-35 A model, with pore size of 0,65 µm, is better than the other one. Both membrane modules present enough protein values to use this treated by-product to a second use. Thus, thinking in large-scale, the first one is the only one which allows an admissible flow value, taking into account the large amount of whey that cheese industry generate.

The result of treating whey using this technology results in a whey protein concentrates and whey isolates of high economical functional properties of its proteins. The utilization of membrane technologies for the production of bovine whey protein concentrates or for purification their components, such as, ß-loctoflobulin or α-lactalbumin, is currently common and of growing economic interest. [33] However, the lack of uniformity in composition and the presence of fat in whey protein concentrates may restrict its use.

Due to the big acceptance of membranes in this kind of treatments, related concentrate a profitable part of by-products, the industry tend to go further. It is visible in next schema, Figure 14, all possibilities of membrane applications from whey.

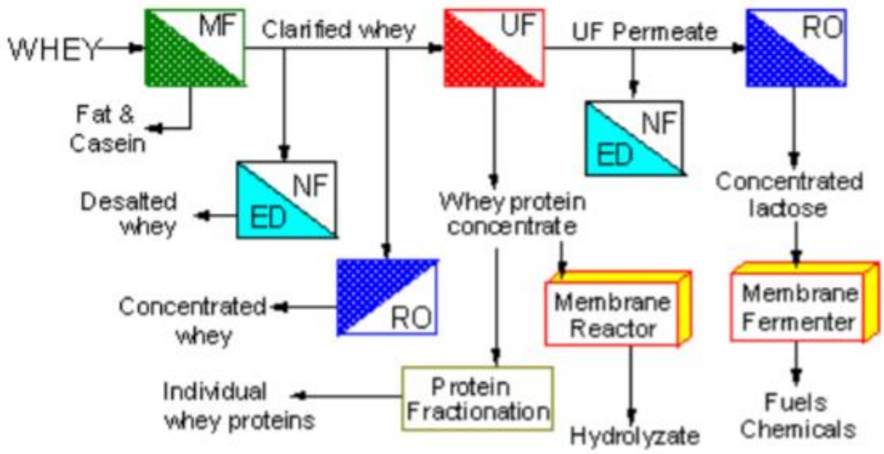


*Figure 16. Whey treatments by membrane technologies.*

## 4.3. Nanofiltration

Due to NF is an especially recent technology, there are not currently too many companies using this technology in its process, and it is pretty limited in an industrial scale. Nevertheless, there are a lot of tests in pilot plants simulating how much benefit will supposed implanting this technology in their lines. That is the reason for explaining why it will be exposed a pilot plant experiment in this chapter.

### *4.3.1. Introduction*

Nanofiltration presents important advantages such as being the intermediate between Ultrafiltration and Reverse Osmosis, providing a separation range between 200 – 1000 Da. Its name comes from the pore size which is 1 nanometer ($10^{-9}$m). Apart from that, the pressure needed to get the separation is 10 – 30 bar, much less than the 80 bar that can be achieved in Reverse Osmosis process.

The appearance of this new technology suppose a new range of applications, and one of the field which has proved to be one of the most beneficial is the water industry, especially in high quality water production. This technology is so attractive due to allow the salt removal in not aggressive conditions. Apart from that, because of the active layer composition, it is vulnerable of saltine solutions and pH, it can have positive, neutral or negative, mainly the last one, guaranteeing a new possibilities of applications.

In recent years, Nanofiltration has achieved a high development level, being designed initially for water softening. Now, its applications are rising, mainly in water treatment such as nitrates separation in subterranean waters, sulphate removal, calcium removal, heavy metal removal, between others.

This technology is on the rise due to, despite it is less selective, it is more effective than Reverse Osmosis in some applications. Nanofiltration selectivity depends mainly on steric effect related to charged groups and solubilization effect. Otherwise, NF can be preferable than RO because of its permeate. For example, in toxic effluent treatments in metallurgical industry, using RO membranes, it will be found a metallic ions rejection greater than 95% and Chemical Oxygen Demand (COD) of 10 ppm in permeate; but, using NF membranes, the reject will be 79% and permeate COD of 35 ppm. Both results of permeate water satisfy the reusing conditions, being Nanofiltration a better option due to its high permeate flux with low pressure. [34]

### *4.3.2. Nanofiltration pilot plant*

As it was commented, because of the limitation of this technology in a large scale and confidentiality of industries, in this chapter is going to see a study of different NF membranes to obtain ultra-pure water and a purpose of replacing RO membranes with NF membranes to obtain WPU (Water for Pharmaceutical Use), using a semi-industrial pilot plant.

In this experience, it was used three commercial NF membranes provided by supplier PCI (Paterson Candy International) and they are the models AFC80, AFC40 and AF30. Membrane type "the film composite" with multilayer structure and asymmetric. Membranes are tubular and they are connected in 18 tubes in series inside of stainless steel modules AISI 316. Total filtration area given by the module is 0,864 $m^2$.

The total membrane thickness is around 500 micros, which can distinguish the polyester support (250 – 280 microns), polisulphone porous layer (220 – 260 microns) and aromatic polyamide active layer (95 – 160 micros).

*Table 4. Some membrane information provided by the manufacturer.*

| Membrane model | Active layer (microns) | Porous layer (microns) | Support layer (microns) | Max. pH range | Max. pressure (bar) | Max. temp (ºC) |
|---|---|---|---|---|---|---|
| AFC30 | 140 – 150 | 240 - 250 | 250 – 280 | 1,5 – 9,5 | 60 | 60 |
| AFC40 | 160 – 170 | 250 – 260 | 250 – 280 | 1,5 – 9,5 | 60 | 60 |
| AFC80 | 95 – 110 | 220 | 260 – 280 | 1,5 – 10,5 | 60 | 70 |

*Feed to be treated*

In selectivity tests, it was used dissolutions of simple salts in proportions 1:1 (NaCl), 2:1 ($CaCl_2$) and 1:2 ($Na_2SO_4$). Although the results will be summarised.

During tests, the feed water to be converted in ultra-pure water, concretely in water for pharmaceutical use (WPU), comes from tap water of the Spanish capital, Madrid, where these experiments have been performed.

*Pilot plant*

The equipment was developed and patented by the Engineering Group of Filtration Processes with Membranes of the Cantabria University (IPFM-UC-Spain).The semi-industrial pilot plant counts with a 150 liters tank and it can perform any membrane process (MF, UF, NF and RO) by standard modules.

These are the main components of the plant:

- Impulsion system: variable pump whose pressure range cover all the different technology needs.
- Variable module adjuster to assure the perfect colocation and performance.
- Measure and control systems (temperature, pressure, pH, flow…).

Moreover, it was designed in order not to adjust any structural part of the pilot plant when it is changed the work range.

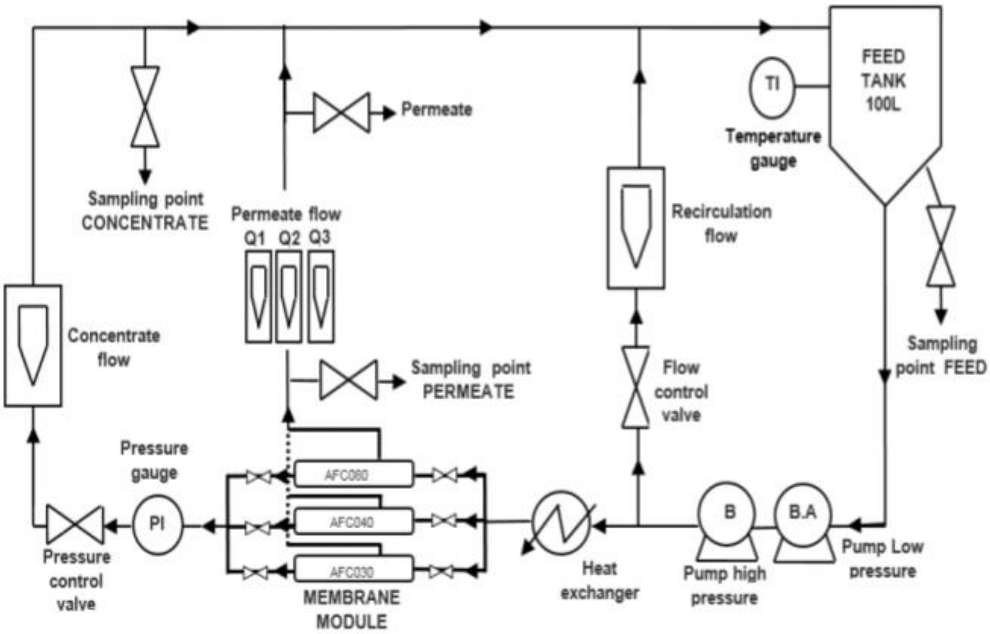


*Figure 175. Representative schema of the pilot plant, where it is shown the modules disposition of membranes AFC80, AFC40 and AFC30. [34]*

In Figure 15, it is visible a schematic flowchart of the pilot plant. It stars in the feed tank on the right. Pumps impulse feed to the membrane modules which are placed in parallel and different valves allowing the selection of what membrane wants to be tested in each case. Membrane are connected between them in order to collect the permeate and concentrate flows, although, in this test, they will be collect separately. Moreover, before the heat exchanger, there is a recirculation current. These three currents return to the feed tank. Besides, there are different valves to take samples in all currents.

*Membrane performance*

This experiments requires a previous study of characterisation of membranes in order to know the parameters that define the membrane behaviour such as permeate flux

($J_p$, $L/m^2h$) and selectivity, defined as rejection (R, %). Thanks to this study, it is easy to predict future applications and separation processes. In addition, to optimise the Nanofiltration membrane process, it is common to perform with different operation conditions (T, P, pH, Qf).

Next, it is presented a representation of the data obtained in characterisation tests for membrane AFC80 where feed was a dissolution of NaCl (0,01M). It is presented once as an example, due to each experiments counts at least with two graphics, and there are quite variables in this experience.

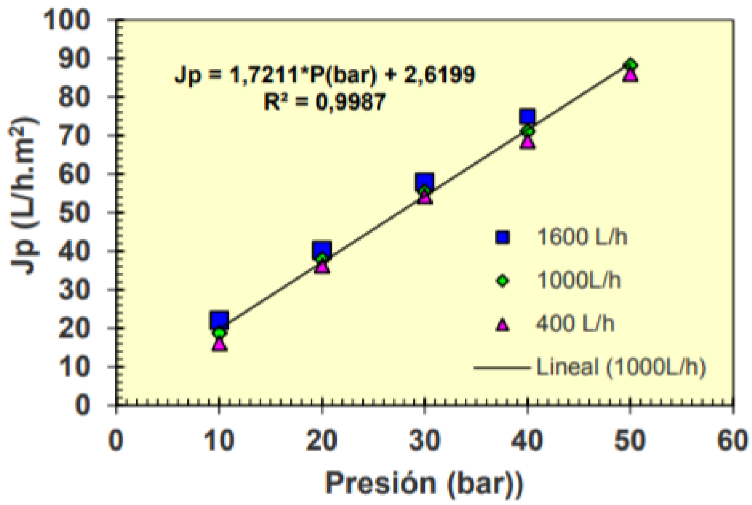


*Figure 16. Variation of permeate flux with pressure in different flows. Membrane AFC80, feed dissolution NaCl 0,01M and T=30ºC. [34]*

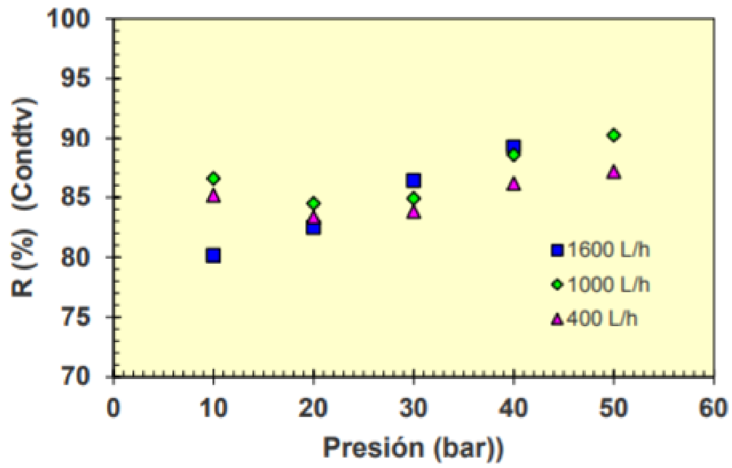


*Figure 187. Variation of rejection rate with pressure in different flows. Membrane AFC80, feed dissolution NaCl 0,01M and T=30ºC. [34]*

For all the membranes, despite it was only presented one example (AFC80, NaCl 0,01M), they have responded as it was expected. All membranes respond to the permeate flux according to the equation $Jp = A \cdot (\Delta P - \Delta \pi)$, giving a straight line, like in

Figure 16. According to the rejection rate, the results are not so predictable, due to the influence of their charge, that it is variable and provide an extra limitation, depending on the feed characteristics and the operation conditions. Rejection rate follow the next equation $R = (1 - Cp/Cf)\cdot 100$, and it is noted that concentrations has been calculated from the conductivity.

Comparative analysis between: AFC80, AFC40, AFC30

In this point, it is important to remember that this experiment was for looking for applications of Nanofiltration to refurbishment of tap water to obtain water for pharmaceutical use (WPU), which is raw material for lots pharmaceutics.

To this end, it is summarise the results during the characterisation process for each membrane:

- Membrane AFC80: Tiny pour size (0,38 nm), slightly negative charge, low productivity (<60 $L/m^2h$ for 40 bar) and very high saline rejection (>96%). It is quite similar resembling an Reverse Osmosis membrane but with better productivity.
- Membrane AFC40: It has a higher pore size (0,44 nm), more negatively charged than AFC80, high productivity (160 $L/m^2h$ for 40 bar) and mild saline rejection (>60%). It is a common Nanofiltration membrane for partial desmineralitation.
- Membrane AFC30: It has the highest pore size (0,51 nm), the most negatively charged, high productivity (190 $L/m^2h$ for 40 bar) and mild saline rejection (>60%). This membrane is also a NF membrane but, with big alkaline earth metals permeability.

*Table 5. Permeate flux and rejection rate of each membrane for these conditions: 30bar, 1000L/h and 300-1000 ppm feed concentration. [34]*

| Membrane | Jp ($L/m^2h$) | R(%) |
|---|---|---|
| AFC80 | >40 | >97 |
| AFC40 | >120 | >70 |
| AFC30 | >160 | >70 |

The general tendency of rejection as permeates flux larger, as a consequence of operation pressure increasing.

After characterization and knowing how membranes works in different conditions, it is the moment to treat with tap water. Moreover, it is available the values to Reverse

Osmosis equivalent membrane for the same purpose, RO-AFC99, in Table 6. The results are exposed in the next tables:

*Table 6. Permeate flux and rejection rate of tap water for tested NF membranes and RO. [34]*

| Membrane | Jp ($L/m^2h$) | R (%) |
|---|---|---|
| NF-AFC30 | 178 | 70 |
| NF-AFC40 | 131 | 71 |
| NF-AFC80 | 52 | 96,6 |
| RO-AFC99 | 35 | 99 |

*Table 7. Relative productivity and selectivity of NF membranes in relation to its equivalent RO membranes. [34]*

| Membrane | Productivity (Jp.NF/Jp.RO) | Selectivity (R.NF/R.RO) |
|---|---|---|
| NF-AFC30 | 5,10 | 0,72 |
| NF-AFC40 | 3,74 | 0,72 |
| NF-AFC80 | 1,48 | 0,97 |
| RO-AFC99 | 1 | 1 |

Seeing the previous results, NF-AFC80 is the most appropriate NF membrane to obtain water for pharmaceutical use. It competes with its rival RO-AFC99, as it has a slightly lower selectivity although it has a 48% higher productivity, supposing a huge energetic and membrane saving, apart from an important installation size, saving for the same purification water volume. The results prove that, for lap water, with a lower conductivity than 800 µS/cm, using two stages in series, the purification water would have an conductivity lower than 1,3 µS/cm, achieving the requirements of all important pharmacological regulations (EEUU, Europe and Japan).

Using the other tested membranes would allow making different configurations with NF-AFC80 and RO-AFC99, in order to optimize the WPU production, recovering and reusing different process currents, especially from the rejection currents, approaching to the main environmental objective for industrial processes: “zero discharge”.

It is shown, in Figure 18, an example of a configuration with tested NF membrane modules.

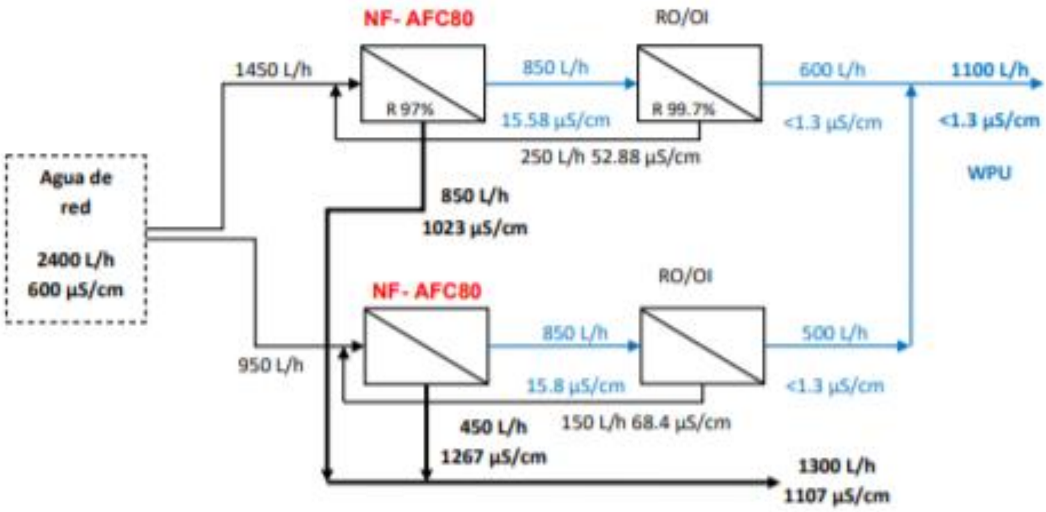


*Figure 18. Example of incorporation of NF membrane (NF-AFC80) in a WPU production process where before they were RO membranes. [34]*

Nanofiltration has an important role in pharmaceutical and biotechnology fields. Their applications are always focus on separation and purification processes of active pharmaceutical ingredients (API) and waste water treatments. Professionals believe that Nanofiltration will have a promising pharmacological future. [35]

## 4.4. Reverse Osmosis

As an example of the technology of Reverse Osmosis in industry scale, it has been selected the "Torrevieja Desalination Plant" where RO represents the heart of the plant where the salt removal takes place.

### *4.4.1. Introduction*

Reverse Osmosis has progressed widely in the last decades and it has passed to be from an emergent technology to an efficient and competitive process. This technology serves in different sectors which may need high quality water or ultrapure water. Some examples could be industries like: food, pharmaceutical, medic, cosmetics, chemicals, electronic, biotechnological, between others, although there is an application where Reverse Osmosis is used worldwide, the desalination.

Desalination is a process where salt (sodium chloride) is removed from seawater or brackish water to obtain safe water. The presence of dissolved salts avoids human consumption and finding a way to remove salts in a viable way had become in an important challenge after the Second World War. [10]

The 97,5% of water present in this planet is salty. The salinity of blackish water is between 2.000 – 10.000 mg salt/L and we can find it in lakes and some seas. Otherwise, seawater presents salinity values of 30.000 – 40.000 mg salt/L. This difference of salinity values allows water industry use Nanofiltration technology for blackish water and Reverse Osmosis for seawater, the most widely used. [23]

Nowadays, this technology is developed enough to obtain huge amounts of drinking water every day and satisfy hundred thousand people demand. In fact, Spain counts with one of the biggest desalination plant in the world, located in Torrevieja (Alicante).

A desalination plant is a complex industrial facility built in the coast proximities in order to catch the seawater easily. It can classify the steps in: water catchment, pre-treatment, Reverse Osmosis and post-treatment for human consuming.

In this type of installations, the most energy consuming equipment is concentrate in high pressure pumps as they have to impulse from sea to the plant a huge amount of water (catchment pumps), taking into account that RO membranes are able to produce not more than 0,5 L drinking water per seawater litre, and supply enough pressure to assure the salt separation (RO pumps).

RO pumps, referred to "high-pressure pump" in Figure 19, consume much less energy that the catchment ones, thanks to ERD (Energy Recovery Devices). There are different types of ERD, but the most common ones, currently, are *pressure recovery*, which uses the high pressure of concentrate flow (brine) to impulse part of the water in feed current, helped by *Booster pump*, decreasing the energy consumed by the RO pump. These ERDs are made by a unique manufacturer company called *Energy Recovery*.

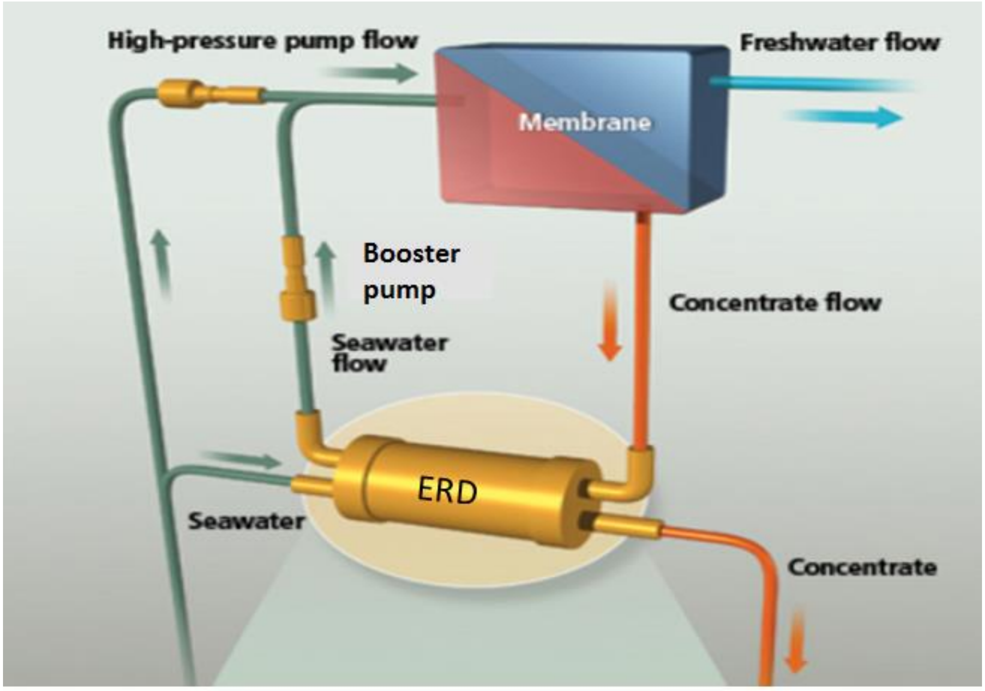


*Figure 19. Schematic mechanism of how ERD connected to a RO system works. [36]*

### 4.4.2. Torrevieja Desalination Plant

Torrevieja Desalination Plant is the biggest desalination plant in Europe, and the second in the world, after the Carlsbad Plant (California, EEUU). It is situated in the southwest part of the city and it has a maximum capacity of 240.000 $m^3/d$, although after a possible extension could achieve approximately 360.000 $m^3/d$. It was built, by the ACCIONA group, with the intention to have alternative hydrological resources to guarantee the irrigation zones of the *Tajo-Segura aqueduct* and *Canales de Taibilla*, apart from the "*La predrera"* reservoir. [36]

According to legal requirements, the irrigation water must achieve these quality parameters:

- Salinity < 400 ppm
- Bore concentration < 0,5 mg/L
- pH between 7 – 8
- Turbidity < 0,4 NTU

Moreover, it requires a landscape integration and solar energy technology (200 kW by photovoltaic panels). Another important aspect which is strictly supervised is the brine discharge. The conversion that RO membranes offer is 45%, in other words, 55% of feed water is pumped again to the sea, using 40 diffusors to ease its diffusion, in order to reduce the environmental impact.

Below, there are the main steps in a Desalination Plant, focus on the Torrevieja plant [37]:

- *Catchment*: Big PRFV pipes are extended 2.000 metres toward the deep sea. First shape limitation by grids for big solids. In the other side, close to the plant, the high pressure pumps which capture 6,38 $m^3/s$.
- *Entrance control*: Before enter to the pre-treatment, there are several controllers to register SDI (Silt Density Index), seaweeds, pH, between others.
- *Pre-treatment*: Different steps in line for assuring the proper physic and chemical conditions before Reverse Osmosis step. Depending on the water conditions, some step can be omitted.
    - *Roughing*: Big solids removal.
    - *Reactive additions:* Sodium hypochlorite (biocide to reduce biological load), sulphuric acid (pH adjustment), barium sulphate (antifouling), ferric chloride (colloid coagulant) and flocculent.
    - *Sand filtration:* Suspension matter removal and SDI reduction. This part is composed by 32 open sand and anthracite filters (3.648 $m^2$ filtration area).
    - *Cartridge filtration*: Security filtration just before the RO phase to assure the protection of the sensitive Reverse Osmosis membranes. This part is composed by 23 vertical filters.
- *Reverse Osmosis*: This phase is the most important where the salt removal takes places. It consists of 16 trains with 7 spiral RO elements in line per tube.
- *Post-treatment*: Re-mineralization in order to achieve the quality requirements according to RD 140/2003 by lime milk and carbon dioxide addition.
- *Final water propulsion*: From the storage tanks, water is impulse to pumping station where will be distributed by more than 20 kilometers of conductions.

Apart from the main steps, there also are other facilities such as sludge treatment, electric installation or control system.

### *4.4.3. Reverse Osmosis phase*

As it has been commented, the Torrevieja Desalination Plant is composed by 16 trains, as it can be appreciated in Figure 20.

Each train is composed by [37]:

- 1 High pressures pump to get the Reverse Osmosis and salt separation.
- 2 Booster pumps connected to 20 ERDs, which allows to recover 0,34 kWh/$m^3$.
- 218 RO tubes which contain 7 spiral modules (Figure 12) inside per tube, which are able to achieve good values of conversion until 43,3%.

Figure 19 is a schematic representation of a train, where "Membrane" is referred to the structure that contains all the tubes per train, visible in Figure 20.

*Figure 20. Torrevieja Reverse Osmosis phase where can be observed the big RO trains connected to the high pressure pumps and the pressure exchangers ERDs. [38]*

In other words, this plant split pre-treatment water into 16 different conductions. These conductions bring water to one of the trains, where it is impulse by high pressure and booster pumps to the different tubes. Each tube has 7 modules in series (to improve the conversion) where water enters to the first module and its concentrate current will be the feed water of the second module. Meanwhile, the permeate currents are collected. It is easily visible in Figure 21.

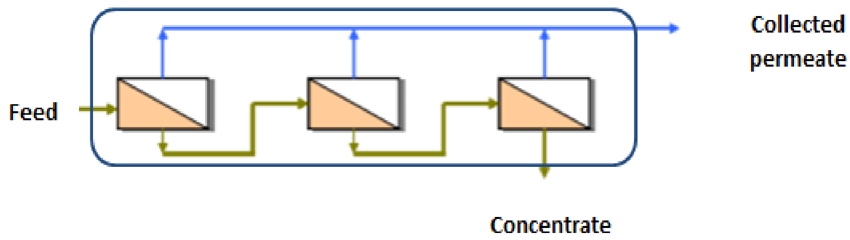


*Figure 21. Schematic tube interior with three modules in lines. [24]*

Moreover, this plant has a Reverse Osmosis train's configuration in two steps. In other words, tubes are connected in such a way that permeate pass through membrane modules twice, thus, when collected permeate leaves the tube, goes to a second tube in order to increase the total recuperation factor, meaning a reduction of seawater for the same production, although desalination plants used to have only one step. [39]

Finally, the concentrate current is impulse more than 2 kilometres until its discharge and permeate is collected (15.000 $m^3$/d/train) and impulse to the post-treatment.

These results make 440.000 beneficiary people and more than 8.000 hectares are covered for irrigation. The priority of the project was to supply drinking water in case of drought but the meticulous design allowed getting the Bore concentration limit (the most common limitation for irrigation water).

Unfortunately, it is not all good news for this facility. Despite the energy recovery devices and the philosophy of working in two steps, Torrevieja Desalination Plant continues to need too much energy to produce drinking water. To get an idea, the minimum energy to produce seawater desalination is 0,78 kWh/$m^3$, but desalination plants used to need at least 3 kWh/$m^3$ in order to compensate all losses (friction, pipes, pums…) but, Torrevieja plant needs 4,74 kWh/$m^3$. Thus, taking into account the high specific energy consumption, Torrevieja is not able to supply so much energy, and the plant is currently used only the 30% of its capacity, supposing that all the treated water was only intended to drink. [40]

# 5. CONCLUSION. FUTURE OF MEMBRANES AND INDUSTRIAL VIABILITY.

Membranes technology is a growing science and each time has more presence in more applications, not only industrial applications but also in ordinary life such as the air filtration system in a building or in a car, food industry (milk, juice, wine, beer…), drinking water purification, sewage treatment between other, as seen above.

Since the decade of 90, when membranes got to be a well-established technology with good efficiency values, they got to substitute much traditional separation processes. And this development was directly coupled with material and polymers improvements. The ability of modify the selectivity properties according to the final applications which will be used has been the best progress.

Apart from that, the material engineering has also supposed an important role allowing the modules production on a large scale with flexibility and with very large filtration areas. The clearest example of this is the huge impact of Reverse Osmosis to produce drinking water from sea water. In fact, Spain is the Mediterranean region with major desalination capacity producing 1 billion of cubic meters of water annually. [28] And, according to energy, Reverse Osmosis and desalination has also the best improvement of energy consumption as modern plants, as it has seen, has an specific consume of 3 – 5 $kWh/m^3$ while traditional thermic processes consume was close to 12 $kWh/m^3$. [24]

Membranes technology have quite advantages: separation process can be performance in series, membrane process can be easily combine with other processes, separation can be taken place in low aggressive conditions, it is easily scalable, in most cases it is not necessary additives use, between others. And this standardised product modules and the ease to combine them allow that, apart from the conventional applications, where is practically always a membrane process,  it can be found, following the same methodology, in a tirth treatment for an specific application, as it has been seen in Benidorm Sewage Treatment Plant. In addition, it also allows to make easily proves in pilot-plants, until the point of using the same pilot-plant for all the membrane technology studied, as it has been seen in the Nanofiltration experience, optimizing the membrane modules to obtain WPU.

Unfortunately, there also are some disadvantages of membranes, such as some membranes life is too short or the high sensitive manufacturing process whose selectivity can be affected in a negative way. Although, the biggest problem of membrane technology is the viability of the process, taking into account whether that high quality permeate worth that investment. Moreover, politics and environmental factors takes part limiting its use and concentrate discharge. As all industrial process, it must consider an economic balance between costs (maintenance, membrane replacement, energy…) and the value that outputs can achieve, that, in some cases, it can be really high.

Currently, membranes are one of the biggest fields widely in investigation due to it has been proved its high potential. The ease of working in series, the ease to operate and the huge variety of membrane modules in the market approach this technology as an standard separation process which high expectative due its good separation results.

Membrane is a technology for the future and it bets for innovation. As an example, the automotive revolution, where in a close future, professional of the sector affirm that electric battery cars will be substitute by combustible cells. Batteries are temporary energy source while combustible cells are energy converters, which can work in continual in presence of combustible, oxygen and hydrogen. Membranes would block the electrons flux, allowing the pass though exchanger's ions between electrodes, apart from avoid the mix between oxidant and combustible.

According to tendencies, sells of membrane equipment will still increase, as it have been registered more than $12.000 million and, in Reverse Osmosis, $4.700 million in 2017, being DOW Chemical the leader in the membrane market, according to The Mckkvaine Co. [9]

To sum up, membrane technology is a really close technology and we don't think in it in an industrial scale, as we can find it in our daily lives: in our breakfast with milk and juice, the packing of our food, our shoes material, in our jacket, when we drink water, beer or wine, or when we breathe in the office. [41]

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