Chapter 2
Overview Membranes Separations

The technology of membranes separation is a field that involves many processes. These processes are subdivided according to the driving force applied, the feeding phases, the permeate, and the pores’ size. The applied driving force is understood as the necessary force for the feeding fluid to cross through the membrane until the permeate. The feeding phases, generally, are found in liquid or gaseous state. Another important aspect, which is considered crucial for the process, is the pores’ size, as many separation processes involve the principle of size exclusion. Figure 2.1 shows the main processes of membrane separation which involve transmembrane pressure as driving force. According to the figure, we can see the pressure regions where microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmose (RO) processes occur, as well as the size of the solute to be excluded for each process and material to be withheld.

In this chapter, the main processes in technology of membrane separation will be discussed succinctly. These processes are MF, UF, NF, and RO. Still, permeation of gas (PG) and the membrane distillation (MD) processes will be presented, in which ceramic membranes have been gained space.

2.1 Membrane Definition

To a better understanding of membranes separation processes, it is necessary to know what is a membrane. The complete and precise definition of membrane can be easily understood, as the synthetic material, which when used turns into a membrane, as well as the process of obtaining present a diversity of aspects to be considered. Generally, a membrane can be characterized as a barrier that separates or restrings partly or totally the passage of existing chemical species due to its characteristics. This membrane can be homogenous or heterogenous, had positive or negative charge, present neutral charge or even, be bipolar, symmetric or
asymmetric, porous or dense and can be composed by various materials. Still, membranes can be polymeric, ceramic or composed. The material which it is done will depend on the necessities imposed and the kind of process to be used.

Figure 2.2 shows a presentation of a membrane and the possibilities which surround it, as, for example, the kind of material, the driving force, diverse existing configurations, the structure, and what is possible to separate.

The species took from the membrane can be called retentate or concentrate, while the species which cross the membrane structure are denominated permeate or filtered. The driving force will be used in membrane separation processes can be a gradient of applied pressure, gradient electric potential or concentration gradient.

2.2 Microfiltration

2.2.1 Microfiltration History

The beginning of microfiltration usage can be dated on the nineteenth century with synthesis of nitrocellulose, in 1845, by Schoenbein. On the following years, in 1855, Fick used colloidium solutions (Ether-alcohol) to form the first nitrocellulose membrane. In 1906, the research in microfiltration membranes continued with Bechold, that obtained porous colloidium membranes and measured the pores size by the bubble point test. In this same century, in around 1925, researchers like Bigelow, Gembering, Schoep, Brown, Zsigmondi, and Bachmann made significant

![Fig. 2.1 Main membrane separation processes, involving transmembrane pressure as driving force (Singh 2006)](image)
advances on methodology of pores sizes’ spreading and regulation. However, despite its high level of sophistication in controlling the size of the pores and microstructure, the authors still have no knowledge of the mechanisms in formation on membrane. The first big and great application of this microfiltration happened in the Second World War, where there was an urgent need for an efficient method as a detection of serious pathogenic bacteria.

After the great war (1947), US Joint Intelligence Objectives Agency sent Dr. Alexander Goetz to Germany to obtain information about the method of production of filter membranes. Goetz visited Membrane filter gesellschaft and based on his discoveries he was awarded with a contract by the US Chemical Corps to develop membranes. In 1950, Goetz had improved the method of membranes production, obtaining higher fluid taxes and more uniformed pore sizes. Based on developments from Goetz, the Lovell Chemical Company in Watertown, Massachusetts, adjudicated more contracts in 1952 to commercialize the production. In 1954, Lovell Chemical Company sold the manufacture to Millipore Corporation and other companies, which started to make membranes according to the German techniques.

### 2.2.2 Microfiltration Process

Microfiltration process can be understood as a technique of separation, able to remove particles with sizes on micrometers scale, as bacteria, yeast cells, colloids,
and suspended particles. The fluid passage with the contaminants will occur through a membrane with pore diameter of 0.1–10 µm. This average of size covers a great variety of natural and industrial particles, as shown on Fig. 2.1. The separated particles in this process are much bigger than the solutes which are separated by reverse osmosis and ultrafiltration, consequently the osmotic pressure is paltry. The driving force in this process is the gradient of pressure formed between the two sides of membrane and can vary from 50 to 200 kPa (Ho and Sirkar 1992).

In this process, the membrane pore size is usually bigger than the processes of ultrafiltration or reverse osmose, consequently the microfiltration process has bigger permeated fluxes. During the microfiltration process, the imposed pressure, which is the driving force to the process, makes the fluid and the smaller diameter go through the membrane and be collected as permeated. The bigger particles are removed by the filtering and collected as concentrate. The mechanism which the particles are removed depends on the kind of filtering and of the kind of interaction with particles to be filtered (Cheryan 1998).

MF process can be done on two different ways: dead-end and crossflow. A classic example of dead-end flux is the use of MF cellulose nitrate or cellulose acetate membranes, diameter 0.45 µm, to the count of bacteria. In this configuration, the feed flux goes to the membrane surface in perpendicularly. As shown in Fig. 2.3, transmembrane pressure obligates the fluid passage through the membrane’s pores, giving a clarified permeate. On dead-end process, the particles tend to accumulate along the filtration process, and, when a solute layer (cake layer) is formed, the permeate flux decreases drastically. As consequence, the filtration

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**Fig. 2.3** Dead-end configuration
process shall be constantly interrupted so that the solute layer is removed or the membrane is replaced (Scott 1998).

Crossflow configuration appeared as an alternative to dead-end configuration. For the crossflow microfiltration the sieve mechanism is seen as dominant of the process. This configuration is often used on ultrafiltration, to the clarification of beverages in the food industry. Still, this configuration, differently from dead-end, is used for a feed with higher quantity of solute. The main advantage of this configuration, compared to dead-end, is the shear force provoked by the fluid which drains parallelly to a membrane surface, which provokes a drag and decrease of the cake layer. Consequently, relatively high permeate fluxes can be achieved and maintained for a long time. According to Fig. 2.4, the constant permeate flux is reached when the cake layer hits a determined thickness. However, in practice, the decrease on permeate flux is observed even when there is no accumulation of solute. Besides, a more commonly used module to the dead-end configuration is the plate and frame module, while, on crossflow configuration, it is the tubular module (Oyama and Stagg-Williams 2011; Meyer et al. 2015).

When the sieve mechanism on the microfiltration is dominant, a cake layer of rejected particles usually is formed on the membrane surface. The permeate flux by the pressure through the cake layer and the membrane can be described by Darcy’s Law, Eq. 2.1.

Fig. 2.4 Crossflow configuration
\[ J = \frac{1}{A} \times \frac{dV}{dt} = \frac{\Delta P}{\mu \cdot (R_m + R_c)} \] (2.1)

where \( J \) is the permeate flux, \( A \) is the membrane area, \( V \) is the permeate volume, \( t \) is the time of the filtration process, \( \Delta P \) is the transmembrane pressure difference, \( \mu \) is the absolute viscosity of the fluid, \( R_m \) the resistance given by the membrane, \( R_c \) is the resistance presented by the cake layer.

In case the membrane gets near a more porous environment formed by spheres which touch tangentially, the permeate flux can be calculated through Carman–Kozeny’s model, Eq. 4.4.

Hydraulic permeability is another parameter to be calculated on microfiltration process. Hydraulic permeability can be understood as a measure of greater or lesser ease which the membrane offers to the passage of a determined solvent, and can be calculated by Eq. 2.2.

\[ L_p = \frac{J}{\Delta P} \] (2.2)

### 2.3 Ultrafiltration

#### 2.3.1 Ultrafiltration History

The concretion of the beginning of ultrafiltration process coincides with the reverse osmose, around 1960. However, the word ultrafiltration emerged in 1856 with Schmidt, which carried out the filtration of proteins and Arabic gum with the usage of a membrane of animal origin. In 1906, Bechold produced collodium membranes with pores smaller than 0.01 \( \mu \)m, made from acetic acid and cellulose nitrate.

The discovery of an anisotropic reverse osmosis membrane, in 1959, opened doors to an anisotropic ultrafiltration membrane. Despite the differences between the membranes, their evolution process was given parallelly. Before that time, Zsigmondy produced one of the first patents in this area, about the preparation of flat collodium membranes. However, these membranes were only a curiosity of the academia, and were applied in the biotechnology area and in laboratory scale.

After the First World War, the American government got worried with water shortage before the end of the century. The United States Department of the Interior created the Office of Salina Water (OSW) and pawned substantial financial resources to the development of various separation processes to the desalination of water, which included processes with membranes. In this time, Loeb and Sourirajan developed asymmetric cellulose acetate membranes, which had smaller thickness, more selectivity and higher permeability rate, which reduced the process time and the permeate area. Besides, these membranes presented macroporous structure, responsible for its higher mechanical resistance.
2.3.2 Ultrafiltration Processes

The ultrafiltration process is a separation process based on the principle of size exclusion. The UF membrane pore size is in average 1–500 nm and is able to retain solutes which present molecular weight from 300 to 500,000 Da. The operating pressure is around 100–700 kPa. UF can reject proteins, such as trypsin, egg albumin and bovine serum albumin. One of the characteristics of UF membranes is your distinction in regards to your molecular weight cutoff (MWCO). Usually, the MWCO set the ability of membrane and rejection occurs when the membrane presents rejection equal or greater of 90%. Despite this present process deletion by particle size, often the membrane may have the ability of retaining smaller particles expected. This is mainly due to the formation of a layer of solute, despite contributing permeate flux decline also contributes in a resistance to passage of the solute. In fact, this characteristic hinders the capacity analysis of rejection of the membrane, so the trials involving the MWCO allow a better understanding of the real efficiency of rejection of the membrane. Other molecules involved in this process are the sugar, biomolecules, polymers, and colloidal particles (Ho and Sirkar 1992; Scott 1998).

The MWCO of any membrane can vary with the chemical characteristics of feed as well as with the factors such as molecular orientation and molecular configuration. However, the nature of the larger molecules that are normally separated by UF leads to significant practical differences between UF and RO processes. As a consequence of higher molecular weight of the species separated into a process of UF, osmotic pressure differentials are smaller. At the same time, the liquid phase diffusivity of these species is also lower. Therefore, the problems of fouling of membrane polarization and by concentration are more significant in UF (Scott 1998).

The permeate flow in UF process is given as Eq. 2.3. The difference of calculating the flow of permeated the process of MF for the UF is on the increase in osmotic pressure, which in the case of UF becomes significant.

\[
Q = \frac{k \cdot (\Delta P - \Delta \pi) \cdot A}{l}
\]

(2.3)

where \( Q \) is the volumetric rate of the solvent through the membrane, \( k \) is the coefficient of permeability of the membrane, \( \Delta P \) is the difference of transmembrane pressure, \( \Delta \pi \) is the osmotic pressure difference across the membrane, the membrane area and \( l \) is the thickness of the membrane. The permeate flow is equal to the ratio of the volumetric rate and membrane area (\( Q/A \)).

The main constraints permeated flow membrane separation processes are extensively studied, because they directly influence the process. These constraints are the polarization by concentration, fouling, and the resistance of the membrane.

The resistance of the membrane is caused by geometrical factors such as pore size and distribution, thickness, hydrophobicity, and membrane hydrophobicity. As
on Eq. 2.4, you can calculate the resistance imposed by the membrane, whereas a new membrane and pure water as feed.

\[ R_m = \frac{\Delta P}{(\mu_w \cdot J_w)} \]  (2.4)

where the index W refers to the properties of water.

Fouling resistance is the sum of the resistances of adsorption, the formation of layer cake and blocking pores. It can be calculated according to the Eq. 2.5, considering pure water flow measured after the filtering process.

\[ R_f = \frac{\Delta P}{(\mu_w \cdot J_{w1})} - R_m \]  (2.5)

where W refers to the properties of water and \( J_{w1} \) concerns permeate flow measured after filtering.

Obtaining the resistance presented by polarizing layer by concentration can be obtained according to Eq. 2.6. To this end, it is necessary to determine the total resistance (RT) presented during the filtration, being the sum of the resistance of the membrane fouling and concentration polarization by layer. The total resistance is determined as Eq. 2.7.

\[ R_c = RT - RF - RM \]  (2.6)

\[ RT = \frac{\Delta P}{\mu_s \cdot J_s} \]  (2.7)

where \( \mu_s \) is the viscosity of liquid (in this case is the solution that contains the solution that will be filtered) and \( J_s \) is the permeate flow measured feed solution.

## 2.4 Nanofiltration

### 2.4.1 Nanofiltration History

The history of NF started around the late 70, when the RO membranes began to operate with a reasonable water flow, operating at relatively low pressures. So, with a reduction in operating pressure, which was traditionally high in RO, it was possible to establish a reduction in energy costs. In this way, membranes with smaller rejections of dissolved components, but with higher permeability to water, if presented with a big improvement for the technology of separation (Hilal et al. 2004). Despite several studies presented at this time, the use of the word
nanofiltration, in commercial, was established by the Filmatec Corporation (in 1980), to define a region between ultrafiltration and reverse osmosis. The NF, also known as loose RO has pores with diameters of about 1 nm. The full definition of NF can be established by a number of features, which are quoted below (Paul and Jons 2016):

- pore diameters of less than 2 nm;
- passage of a significant amount of monovalent ions;
- substantially larger divalent ion rejection than monovalent;
- the molecular weight cutoff (MWCO) for neutral species is in the range of 150 and 2000;
- the rejection of neutral and positive ions refers mainly to size and shape.

In fact, the membranes with selectivity in the regions between UF and RO already existed in the years 60, however were termed as open, loose, low-pressure RO, intermediate RO/UF, or tight UF membranes. However, only from the years 80 the word nanofiltration became used firmly and explicitly used by several authors (Wang et al. 2011). Thus, different RO membranes, which have non-porous structure and a transport mechanisms for diffusion, NF membranes operate on porous and non-porous membranes interface, prevailing the mechanisms of diffusion and deletion by particle size.

2.4.2 Nanofiltration Process

In NF, as well as other membrane separation technologies, mass transit can lead to binding, accumulation or absorption of materials on the surfaces of the membrane and/or within the porous structure, causing a decline on the permeated flow throughout the period. The consequence of that, is the decrease of permeability and the need to increase the transmembrane pressure to maintain the desired flow, in addition to increased energy consumption, operating costs and increase the frequency of cleaning. Cleaning the membrane is the main form of mitigation of polarization layer formation by merger, the formation of gel layer and the effects of the phenomenon fouling, but a loss will occur in the lifetime of the membrane (Mohammad et al. 2015).

NF membranes exhibit an active layer, where the rejection occurs, which features pores with nanometer geometry, and can be characterized by different techniques. The main techniques used are those of gas adsorption and desorption, atomic force microscopy, transmission electron microscopy (TEM), and rejection of solutes. The hydrophilic/hydrophobic properties are constantly evaluated in this type of membrane for presenting important relevance of the membrane interaction with the solvent, which can be determined with relatively inexpensive techniques (Mohammad et al. 2015).
Another important feature presented by the membranes are the loading properties, which are the key to the understanding of the process and this variable depends on the nature, concentration, and pH of the solution. These electrical characteristics allow an increase in mass transport through the membrane and are significant in rejection of the solute (Wang et al. 2011). The NF membrane in contact with the aqueous solution are slightly charged due to the dissociation of functional groups or surface adsorption of solute. For example, NF membranes contain ionizable groups polymer such as carboxylic groups and sulfonic acid groups resulting in a charged surface in the presence of a feeding solution. Similar to the RO membranes, NF membranes are potent in the separation of inorganic salts and small organic molecules (Mohammad et al. 2015).

As well as the fouling, another drawback of NF membrane is the problem of controlling the reproducibility of the size and distribution of pores in the membrane (Wang et al. 2011).

The Nernst–Planck equation, Eq. 2.8, is extensively used to measure the transport of ionic species through the membrane pores of NF. The application of this equation was originally proposed by Schlogl for description of electrolyte transport in RO through ion exchange membranes. The equation is particularly useful for NF, once consideration is given to the transport mechanisms and parameters required, based on the properties of a real membrane. When considering the movement of unidirectional composites by membrane, and assuming ideal solutions, the transport equation for the species i can be written as (Chaabane et al. 2007):

\[
\dot{j}_i = -\frac{C_i K_{i,d} D_{i,∞}}{R T} \frac{d\mu}{dx} + K_{i,c} C_i V
\]  

(2.8)

where \(\dot{j}_i\) is the ionic flow, \(C\) is the concentration, \(V\) is the velocity of the solvent and \(K_{i,d}\) and \(K_{i,c}\) are the obstacle factors to explain convection and diffusion within a confined space.

There are several variations of the equation that models the NF membrane transport. However, the proposed models are based on the Nernst-Planck equation and are variations based on a methodological solution, implications or extensions as the particular parameters (Mohammad et al. 2015).

Despite being the main polymer materials used in the preparation of NF membrane, some authors have reported the use of ceramic membranes for this purpose. Ceramic membranes of NF mainly use materials of titania, zirconia, silica-zirconia, hafnia, and alumina. Most of these nanofiltration membranes were prepared for the separation of non-aqueous solvents using sol-gel process, in which a mesoporous ceramic support is coated with a layer of a metallic oxide that determines the final size of the pores in the active layer. This procedure provides a great advantage in the pore diameter control through the appropriate choice of colloidal solutions at the stage of final coat. The molecular weight cut-off presented by these membranes is located between 200 and 1000 Da (Gitis and Rothenberg 2016).
2.5 Reverse Osmosis

2.5.1 Reverse Osmosis History

The first observations of the osmosis process were held in the eighteenth century, with studies of Nollet and Dutrochet. While these authors contributed to the first steps of the methodological observations involving membrane permeation, Fick and Graham, 1855 and 1866, respectively, were permeant species could be differentiated rates in transport across the membrane. Later, the osmotic pressure measurements were performed by Traube in 1867 and Pfeffer in 1877 and, in 1887, Van’t Hoff used these concepts to explain the behavior of ideal solutions diluted. Reverse osmosis is a well-established technology of water purification, using semi-permeable membranes in the removal of ions and molecules of low molecular mass. The largest application of this process is for the desalination of water for consumption (Wang et al. 2011).

For decades, many authors have reported several studies involving the processes of osmosis and reverse osmosis. In 1959, in the work of Reid and Breton, with cellulose acetate films, it was possible to achieve values of 99% salt rejection of the water, however the permeate flows obtained were considered impractical at the time, reaching a maximum of 1.17 L/m² (Reid and Breton 1959). Still, these authors verified the influence of thickness of selective retention efficiency skin and permeate flow. In the following years, in 1962, Loeb and Sourirajan reported on their studies a high salt rejection with streams of water permeated movies using relatively high cellulose acetate. These studies, among others, formed the basis for the understanding and improvement of the process of reverse osmosis in later years.

2.5.2 Reverse Osmosis Process

When two solutions with different concentrations of solute are separated by a semipermeable membrane, is established a chemical potential difference. Of course, the phenomenon of osmosis is the diffusion of water through a semi-permeable skin to a region of lower concentration (greater chemical potential) to a region of higher concentration (lower chemical potential), until the chemical equilibrium is reached. To achieve the balance the difference in pressure between the two sides of the membrane is equal to the difference in osmotic pressure. To perform the reverse process it is necessary to apply a pressure difference greater than the osmotic pressure, which allows the separation of solute solvent. This phenomenon is called Hyperfiltration or reverse osmosis, Fig. 2.5 (Metcalf and Eddy 2014).

The following equations are used to describe the permeate flow submitted by RO membranes, as well as the calculation of the area of membrane and the number of stages required for a given application (Metcalf and Eddy 2014).
\[
J = k \cdot (\Delta P - \Delta \pi) = \frac{Q_p}{A} \tag{2.9}
\]

\[
\Delta P = \left(\frac{P_f - P_c}{2}\right) - P_p \tag{2.10}
\]

\[
\Delta \pi = \left(\frac{\pi_f - \pi_c}{2}\right) - \pi_p \tag{2.11}
\]

where \(J\) is the permeate flow (m\(^3\) m\(^{-2}\) h\(^{-1}\)), \(k\) is the mass transfer coefficient for the stream of water (depending on the water temperature, the characteristics of the membrane and the solute) (m\(^3\) m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)), \(\Delta P\) is the difference of applied pressure (bar), \(P_f\) is the feed pressure (bar), \(P_c\) is the concentrated pressure (bar), \(P_p\) is permeated pressure (bar), \(\Delta \pi\) is the osmotic pressure (bar), \(\pi_f\) is the osmotic pressure of feeding (bar), \(\pi_c\) is osmotic pressure of concentrated (bar), \(\pi_p\) is the osmotic pressure of the permeate (bar), \(Q_p\) is permeated flow (m\(^3\) h\(^{-1}\)), and \(A\) is the area of the membrane (m\(^2\)).

In most cases, the solutes will pass through the membrane. This way, the solute flow can be calculated by Eq. 2.12 (Metcalf and Eddy 2014).
\[ J_S = k_S \cdot \Delta C_S = \frac{(Q_P)(10^{-3} \text{ m}^3 \text{ L}^{-1}) \cdot C_P}{A} \quad (2.12) \]

\[ \Delta C_S = \left( \frac{C_f - C_c}{2} \right) - C_p \quad (2.13) \]

where \( J_S \) is the solute mass flux (g m\(^{-2}\) h\(^{-1}\)), \( k_S \) is the mass transfer coefficient for the solute (m h\(^{-1}\)), \( Q_P \) is permeate flow (m\(^3\) h\(^{-1}\)), \( A \) is the area of the membrane (m\(^2\)), \( C_P \) is the concentration of solute in permeated, \( \Delta C_S \) is the variation of concentration of solute through the membrane (g m\(^{-3}\)), \( C_f \) is the concentration of the solute in the feed (g m\(^{-3}\)), and \( C_c \) is the concentration of solute in concentrated (g m\(^{-3}\)).

The osmotic pressure, for sufficiently dilute solutions can be calculated by Eq. 2.14. This equation was proposed by van't Hoff, a time to observe the osmotic pressure found that this had a similar behavior to an ideal gas. However, as the ideal gas equation to account for factors fixes for real gases, the van't Hoff equation allows, by van't Hoff factor, the fix for real solutions, Eq. 2.15.

\[ \Delta \pi = n \cdot R \cdot T \cdot i \quad (2.14) \]

\[ i = 1 + \alpha \cdot (q - 1) \quad (2.15) \]

where \( \Delta \pi \) is the osmotic pressure (Pa), \( n \) is the solute concentration (mol m\(^{-3}\)), \( R \) is the ideal gas constant (8.314 Pa m\(^3\) mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature of the solution (K), \( i \) is the correction factor of Van't Hoff, \( \alpha \) is the degree of ionization, and \( q \) is the total number of ions released in the ionization of a compound.

Reverse osmosis is classified into three categories: The first, named RO, is for processes that involve high pressures, 5.6–10.5 MPa. The second involves low pressure processes of 1.4–4.2 MPa, and is called reverse osmosis. The osmosis of low pressure is applied on the desalination of brackish water. Finally, the third category is called nanofiltration or loose RO and operates at pressures from 0.3 to 1.4 MPa (Ho and Sirkar 1992). The nanofiltration was discussed in the previous chapter.

Currently, RO membranes are made of polymeric materials, such as cellulose acetate and polyamide. The most important are the membranes of acetate cellulose with homogeneous asymmetric morphology, the polyamide obtained by phase reversal and the cross-linked thin film composite (TFC) polyamides. Both the cellulose acetate membranes and polyamide possess a combination of economically viable high rejection and water flux. TFC membranes have higher added value than cellulose acetate membranes, but have higher flow and, therefore, operate at a lower pressure (Singh 2006; Lee et al. 2011).

The surface of the polymeric membranes of RO is considered non-porous, consisting of a polymeric network in which the solvent can be dissolved. RO membrane has a dynamic structure that allows the entry of water molecules. In fact, the dense skin has pores that are considered transitional channels. The main
problems associated with polymeric membranes of RO is the excess fouling due to poor feed flow hydrodynamics, low resistance to oxidizing agents (such as chlorine), extensive use of pretreatment and chemicals associated with the generation of waste and lack of surface charge to reduce the fouling (Li 2007; Wang et al. 2011). Another problem associated with RO membranes is the decrease in the flow of permeated the solvent, a result of accumulation of solute molecules on the surface of the membrane, contributing to the increase in osmotic pressure and, as a result, the increase in energy costs.

Tubular and plate modules were the first modules used in the processes of RO. However, due to the low density packaging, these were replaced by modules that allow a higher ratio between the area of the membrane and the volume of the module. Currently, the most widely used are the hollow fiber and spiral wound modules, because they have the highest density packaging, which allows a considerable gain in the permeate flow. However, these modules feature ease of clogging and difficulty of cleaning.

Despite several advantages presented by ceramic membranes compared to the polymeric membranes, as resistance to oxidizing agents and solvents, high pressures resistance and among others; the costs involved in obtaining, low ability to retain ions and molecules of low molecular mass and low density of packaging make unfeasible the use of these membranes in the RO process.

On Li and collaborators’ paperwork, the authors conducted a study using MFI-type zeolite membranes supported with α-alumina with the purpose of purification of water by the process of RO (Li et al. 2004). In this study, the authors found that the ion rejection and the flow of water depend on the charge density of the ions, the size and dynamic of hydrated ions diffusivity. Yet, the authors obtained as a result, for a 0.1 M solution of sodium chloride, with flow of 0.112 kg m\(^{-2}\) h\(^{-1}\), a rejection of Na\(^+\) of 76.7\%, with transmembrane pressure applied to 2.07 MPa. In addition to NaCl, the authors evaluated the rejection of NH\(_4\)Cl, KCl, CaCl\(_2\), and MgCl\(_2\), getting rejections between 58.1 and 88.4\%. Zeolite membranes have been mainly applied in gas separation and liquid pervaporation processes, but recently, dynamic simulation studies have shown that zeolite membranes are theoretically applicable in RO processes and can reach salt rejections of up to 100% (Lee et al. 2011).

2.6 Gas Separation

2.6.1 Gas Separation History

The major milestones of the process of separation of gases are, in large part, on its findings, mainly, of the characteristics and behavior of gases when applied to different pressures and temperatures.
The history of separation of gases can be dated from the findings of a French physicist called Guillaume Amontons in Thermometry and mathematics, which led to his assumption of absolute zero. In 1720, Gabriel Daniel Fahrenheit developed the idea of a temperature scale, which took your name. The Swedish Anders Celsius in 1741, formulated the temperature in degrees centigrade, where zero represents the freezing of water and 100 °C the temperature at which the water boiled. In this same century, the scholar Joseph Priestley managed to isolate a gaseous compound unknown, which Lavoisier later found to be oxygen, one of the ingredients of the Earth's atmosphere. Priestley also found ammonia, sulfur dioxide, nitrogen gas and later identified as carbon monoxide (Yampolskii and Freeman 2010).

In the nineteenth century, it was possible to liquefy industrial gases and check their behavior and characteristics. In 1823, Michael Faraday, would liquefy chlorine and studied the liquefaction and the characteristics of the ammonia. In the nineteenth century, it was possible to liquefy industrial gases and check your behavior and characteristics. In 1823, Michael Faraday, would liquefy chlorine and studied the liquefaction and the characteristics of the ammonia. In 1824, Sadi Carnot presented in his thesis findings which revealed that a thermal engine was more efficient, operating at your ideal, when two tanks (one hot and one cold) were used. In 1845, Thomas Andrews managed to establish the first isotherms, evaluating the behavior of the carbon gas at different temperatures and pressures. He found that the carbon gas could be liquefied with its cooling, independently of the applied pressure. During the years 1850 and 1851, William Thompson and Rudolf Clausius, respectively, articulated the first and the second law of thermodynamics. The first patent for a refrigerating system was deposited in 1951 by a doctor named John Gorrie. These and other discoveries were crucial to the understanding of the behavior and characteristics of the gases, still formed the basis for the separation of gases developed in the following years (Yampolskii and Freeman 2010). In 1983, Bird presents the first results, involving carbon molecular sieve membranes, of the first measures of mass transfer and fluid gaseous diffusion through membranes. In 1985, William Schell presented in his work using gas separation membranes permeability and selectivity results of two different membranes of dimethyl silicone and other cellulose acetate. Still, it was found that the numerous advantages presented as high flux and selectivity in comparison with conventional methods (Schell 1985). These studies, as well as others, were pioneers in the area, and initiated a new application of the membrane technology.

2.6.2 Gas Separation Process

Gas mixtures can be separated by dense or porous ceramic membranes (Li 2007). Several researches have shown, effectively, the use of ceramic membranes in separation of gas mixtures. Ceramic membranes used in the separation of gases can be silica (Nwogu et al. 2016), kaolinite (Hubadillah et al. 2016), zeolite (Chew and Ahmad 2016; Kida et al. 2017), alumina (Donelson et al. 2014), Titania, zirconia
The dense ceramic membranes are made of crystalline ceramic materials, such as perovskite or fluorite, which allow only oxygen or hydrogen permeation through their crystalline structure. So are mostly impermeable to all other gases, giving extremely high selectivity for oxygen or hydrogen (Li 2007).

The quantitative measurement of the gas transport is the flow or the rate of permeation, which is defined as the number of molecules that pass through a unit area per unit time. The flow \((J)\) follows the law of Fick, Eq. 2.16, and is proportional to the concentration gradient across the membrane, that is, there is a movement of gas from regions of high concentration to areas of low concentration.

\[
J = -D \frac{dC}{dX}
\]  

(2.16)

\[
J = D \frac{C_2 - C_1}{L}
\]  

(2.17)

where \(D\) is the diffusivity, \(C(X)\) is the concentration, \(X\) is the position within the structure of the membrane, \(C_1 = c(0)\), and \(C_2 = C(L)\) and \(L\) is the thickness of the membrane (cm). Assuming a linear concentration gradient across the membrane, the flow can be approximated by Eq. 2.17.

The membrane performance of various materials is commonly compared by using the independent thickness material, the permeability \(P\), which is related to the flux \((J)\), Eq. 2.18.

\[
P = \frac{Q \cdot L}{A \cdot (p_2 - p_1)} = \left(\frac{C_2 - C_1}{p_2 - p_1}\right) \cdot D
\]  

(2.18)

where \(P\) is the permeability in Barrer (1 Barrer = \(10^{-10}\) cm\(^3\) (STP) cm cm\(^{-2}\) s\(^{-1}\) cmHg), \(Q\) is the permeate flow rate (cm\(^3\) s\(^{-1}\)), \(A\) is the area of the membrane (cm\(^2\)) and \(p_1\) and \(p_2\) are the pressures (cmHg) permeate side and food, respectively, Fig. 2.6.

If the upstream pressure \((p_2)\) is much larger in relation to the downstream pressure \((p_1)\) the Eq. 2.18 can be simplified in Eq. 2.19.

\[
P = \frac{C_2}{p_2} \cdot D
\]  

(2.19)

\[
P = S \cdot D
\]  

(2.20)

By introducing a solubility coefficient \(S\), the concentration ratio on \(C_2/p_2\) pressure when the sorption can be represented by Henry, Eq. 2.20.

The separation of a mixture of molecules A and B is characterized by selectivity or ideal separation factor, and can be calculated by the Eq. 2.21. The selectivity is represented by the ratio of the permeability of the component by component B permeability.
Currently, several studies indicate the ceramic membranes as alternative hydrogen purification. Hydrogen has been an alternative to fossil fuels because it is considered a green technology, which can in future represent a considerable reduction of the air pollution degree. However, the main difficulty in separating hydrogen from other gases like N₂, CO₂ and CH₄, it is own very small dimension of atoms of gases, as well as in the proximity between the different gas molecules. For the separation to be effective it is necessary to have a control of porosity of selective layer or use of mechanisms that favor the separation. Because of this, some jobs present alternatively the use of palladium as a catalyst of hydrogen dissociation. However, the cost and complexity still are high. On the other hand, these difficulties have led the study of recovery of ceramic membranes used to support selective layers of palladium (Hu et al. 2011; Li et al. 2015).

2.7 Membrane Distillation

2.7.1 Membrane Distillation History

The early history of the Membrane Distillation (MD) is marked with your first patent deposited in 1963, by Bodell. In 1967, with the work of Findley, it was possible to access the first MD. Then, for about a decade, then was a lack of interest of researchers by MD, because there was no suitable membranes still for this process. The process of MD gained momentum again in the 80, when the first porous membrane of polytetrafluoroethylene (PTFE) began to be available on the market. Over the years, until 2013, there was an increase of approximately twenty...
times the number of publications, and in 2016, the number of publications was 442, which is almost five times more compared to the year 2013 (Khayet 2011; Basile et al. 2015).

### 2.7.2 Membrane Distillation Process

Most of the transports that occur in membranes is isothermal and its driving forces are differences in pressures, concentrations, electrical or chemical potentials. In simplified form, the MD is a thermal separation process that distills water. The process of MD is similar to conventional distillation, since both technologies are based on steam/liquid equilibrium for separation. Both processes require the use of heat in feed current. In the process, use a non-isothermal membrane with hydrophobic characteristics, porous, and this is not wet by the liquid streams. The steam heat transport through the membrane occurs by a difference in steam pressure (driving force) between the two sides of the porous membrane. The membrane is maintained in direct contact with the hot liquid feed solution to be treated. In the MD process occurs, at the same time, the mass and heat transfer (Khayet 2011; Alkhudhiri et al. 2012; Drioli et al. 2015; Basile et al. 2015). The MD can have different settings, namely:

**Direct Contact MD (DCMD)**

In this configuration, the difference in vapor pressure is achieved through a temperature difference between the two sides of the membrane, permeated and feed. As the cold liquid (permeated) flows from one side of the membrane, in order to condense the steam that runs through the pores of the membrane, the hot liquid (feed current) flows to the other side of the membrane. This setting can present high flows, but occurs a high loss in heat, and it provides a low efficiency (Hwang et al. 2011).

**Air Gap MD (AGMD)**

In the AGMD process, a gap of stagnant air is maintained between the membrane and the channel of the condenser using a condenser foil. The air gap acts as a layer of insulation. As a result, the heat loss due to driving, that is intrinsic to the DCMD, is noticeably reduced in this configuration. You can also separate the chains of volatile compounds even before mixing with the permeated. In addition, the AGMD enables retrieval of latent heat without the presence of an external heat exchanger. However, the existing barrier (air gap) causes a reduction of mass transfer through membrane (Duong et al. 2016).

**Vacuum MD (VMD)**

The VMD contains a setting that has a channel with an air gap. The membrane is used as a surface for the water to be evaporated in a vacuum environment,
maintained by steam absorption by a desiccator. The advantage of this configuration is that the inert gases do not dissolve, which block the pores, are aspirated by vacuum, leaving the effective membrane area available. Entertaining, the cost of the vacuum equipment and your adaptation to the system can cost a higher price (Chen et al. 2015).

**Sweeping Gas MD (SGMD)**

The SGMD, also known as air stripping, uses a configuration with a channel with empty space permeate side. The SGMD process is mainly used in removing volatile compounds. The feed solution is heated to the desired temperature and transferred to the surface of the membrane. While going through the pores in the direction of the permeated, volatile compounds are dragged by a gas transporter, which leads them to the further processing (extraction). Meanwhile, the non-volatile compounds remain recirculating in the feed. The advantage of this configuration in relation to AGMD is the reduction of additional mass transfer barrier and so could be achieved a higher flow. However, the gas flow can reduce the driving force (steam gradient across the membrane) due to the heating of the gas itself (Duyen et al. 2016).

**Vacuum Multi-effect MD (V-MEMD)**

The technology of memsys vacuum-multi-effect-membrane-distillate, as it is known, combines the advantages of multiple effect and vacuum to achieve efficient heat recovery. The V-MEMD is composed of a steam raiser, stages of evaporation-condensation and a capacitor. Each stage retrieves the heat of condensation, promoting a designer of multiple effect. The thermal energy produced by external heating source (for example, solar heat or other waste heat) is changed in steam raiser. The water from the evaporator is under pressure (for example, 600 mbar). The hot steam is generated by steam-raiser flows to the stage 1, while the feed current is also introduced in stage 1 and flows in series through the remaining stages. At the end of the last stage, the feed is concentrated as brine. The vacuum is always applied alongside permeated the membranes. The vapor pressure and temperature decrease gradually from steam raiser to the condenser. The steam produced in the final stage is condensed in the condenser, using a refrigerant flow (for example, fresh water) (Zhao et al. 2013).

DCMD configuration is the most studied, although the heat transferred by conduction through the membrane, considered the heat lost, is larger in relation the other settings. Almost 60% of the studies of the process of MD are conducted using DCMD systems. On the other hand, is a smaller configuration SGMD use (less than 5%), because external capacitor is required to collect the permeated, complicating the design of the system and increasing your cost (Basile et al. 2015).

One of the main features is the process of MD is the liquid entry pressure (LEP) of the membrane, and this must be greater than hydrostatic transmembrane pressure applied. The LEP is the minimum required for transmembrane pressure water or feed to enter the pore solution, surpassing the hydrophobic membrane
forces. The LEP is related to the maximum pore size \((d_{p,\text{max}})\) membranes by means of Laplace's equation, Eq. 2.22.

\[
\text{LEP} = \left| \frac{4 \cdot \pi \cdot \sigma}{d_{p,\text{max}}} \cdot \cos \theta \right| \tag{2.22}
\]

where \(\alpha\) is the geometric factor the greater the membrane pore, \(\sigma\) is the surface tension of the liquid solution and \(\theta\) is the angle of contact between the liquid and the surface of the membrane.

A membrane with a value of LEP high can be developed using materials of low surface energy or with high hydrophobicity and small pore size. However, when a membrane displays a small pore size is expected to be a low permeability of the membrane. Besides, the size of your distribution and pore is considered crucial in the process of MD. The pore size can vary from 5 nm to 10 \(\mu\)m, however your distribution should be as close as possible.

The Knudsen number \((Kn)\) is another key parameter in MD, and is used to determine the mass transport through membrane pore. Equation 2.23 presents the Knudsen number math definition, and is used under certain conditions.

\[
Kn = \frac{\lambda_i}{d_p} \tag{2.23}
\]

\[
\lambda_i = \frac{k_B T}{\sqrt{2 \pi P_m \sigma_i^2}} \tag{2.24}
\]

where \(\lambda_i\) is average free path of the molecules of steam carried through the pores of the membrane with a \(d_p\) size (Eq. 2.24), \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(P_m\) is the average pressure within the pores of the membrane, and \(\sigma_i\) is the collision diameter.

When it comes to a binary mixture, the value of \(\lambda\) can be calculated using the Eq. 2.25.

\[
\lambda_{i/j} = \frac{k_B T}{\pi P_m \cdot ((\sigma_i + \sigma_j)/2)^2} \cdot \frac{1}{\sqrt{1 + M_j/M_i}} \tag{2.25}
\]

where \(\sigma_i\) and \(\sigma_j\) are the collision diameters and \(M_i\) and \(M_j\) are the molecular masses of the molecules \(i\) and \(j\), respectively.

The Knudsen number is the basis to determine the permeability and permeate flow to various process conditions. Several studies present models to determine the permeability and the permeate stream, but here will not be dealt with these models. For more informations, it is recommended the consult of recommended literature (Basile et al. 2015).
The process of MD uses organic and inorganic membranes. Several studies using ceramic membranes composed mainly of zeolite, zirconia, alumina, and Titania (Fang et al. 2012; Kujawski et al. 2016; Garofalo et al. 2016; Fan et al. 2017). The various advantages of ceramic membranes with polymer make them interesting in the process of MD.

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