



UNIVERSITAT DE
BARCELONA

Treball Final de Grau

Membrane technology for the recovery of nutrients in wastewater

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June 2023

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Reconeixement–NoComercial–SenseObraDerivada



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La vida és com un llapis que segur s'acaba. Però deixarà la bella escriptura de la vida.

One Piece.

El meu agraïment al Dr. Labanda per l'ajuda, per les petites classes d'introducció a les membranes i per la paciència. També, voldria agrair a la Shirin per l'acompanyament al laboratori i l'aportació de coneixements.

Infinites gràcies a la meva parella, la Bitxeta i els meus pels ànims, la motivació i per estar sempre aquí.

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SUMMARY

The main problems are ammonium and phosphate, which are present in many nutrients for animals and plants. The large farms that have grown in recent years, especially slurry, are fed with a high nitrogen content and eliminate it in nature in the form of urea. Most of the urea is composed of ammonium and leaches into the soil, where it can also end up contaminating the water. This situation creates the need for water purification. Reverse osmosis membrane technology is a possibility.

The study consists of the permeation of ammonia using a reverse osmosis membrane. First, the membrane performance was characterized by permeation of pure water and NaCl solutions at different temperatures. The different alkaline media were made for NaCl with the same purpose. In addition, the solute transfer coefficient was estimated to evaluate the effect of polarization. Subsequently, the permeation of ammonia to different effluents was evaluated, as well as solutions of NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$. Moreover, the influence of temperature and pH on water permeability was quantified. Likewise, the permeability of ammonium and ammonia under these conditions was investigated. The ammonia nitrogen transfer coefficient was also estimated.

At the end of the investigation, it could be demonstrated that both solute and water permeability increase with increasing temperature, since it follows the Arrhenius equation. On the other hand, the influence of pH is related to the equilibrium of the reaction. As the alkalinity of the media increases, more ammonia is formed and permeates the membrane. In contrary, ammonium ions hardly permeate and will be retained in the membrane. Also, the transfer coefficient was obtained, and it was deduced that it presents moderate polarization.

This study takes a small step forward in reverse osmosis membrane technologies. As well as innovating, improving, researching, and developing new membrane structures to expand their industrial applications. In addition to improving water quality, ammoniacal nitrogen could be recovered at $\text{pH} > 10.5$ in the permeate. Thus, it could be used as a raw material for many chemical industries.

Keywords: ammonia permeability, membrane performance, polarization, recovery, reverse osmosis.

RESUM

Els principals problemes són l'amoni i el fosfat, que estan presents en molts nutrients pels animals i les plantes. Les grans explotacions que han crescut els darrers anys, especialment els purins, s'alimenten amb un alt contingut de nitrogen i l'eliminen a la natura en forma d'urea. La major part de la urea està formada per l'amoni i es filtra al sòl, on també pot acabar contaminant l'aigua. Aquesta situació crea la necessitat de purificar-la. La tecnologia de membrana inversa és una possibilitat.

L'estudi consisteix en la permeació d'amoniàc utilitzant una membrana d'osmosi inversa.

En primer lloc, es va caracteritzar el rendiment de la membrana mitjançant la permeació d'aigua pura i solucions de NaCl a diferents temperatures. Es va realitzar diferents medis alcalins pel NaCl amb el mateix propòsit. A més, es va estimar el coeficient de transferència del solut per avaluar l'efecte de la polarització. Posteriorment, es va avaluar la permeació de l'amoniàc a diferents efluent, així com solucions de NH_4Cl i el $(\text{NH}_4)_2\text{SO}_4$. A més, es va quantificar la influència de la temperatura i del pH a la permeabilitat de l'aigua. Així mateix, es va investigar la permeabilitat de l'amoni i de l'amoniàc sota aquestes condicions. També es va estimar el coeficient de transferència del nitrogen amoniacal.

Al final de la investigació, es podria demostrar que tant la permeabilitat del solut com l'aigua augmenten amb l'increment de la temperatura, ja que segueix l'equació d'Arrhenius. D'altra banda, la influència del pH està relacionada amb l'equilibri de la reacció. En augmentar l'alcalinitat del medi, forma més amoniàc i aquest permea a la membrana. En canvi, els ions d'amoni gairebé no permeen i es quedaran retingudes a la membrana. També, es va obtenir el coeficient de transferència i es va deduir que presenta polarització moderada.

Aquest estudi fa un petit pas més a les tecnologies de membranes d'osmosi inversa. Així com, innovar, millorar, investigar i desenvolupar noves estructures de membranes per ampliar les seves aplicacions. A més de millorar qualitat de l'aigua, el nitrogen amoniacal es podria

recuperar a $\text{pH} > 10.5$ al permeat. Així doncs, es podria aprofitar com a matèria prima per a moltes indústries químiques.

Paraules clau: permeabilitat de l'amoniac, rendiment de la membrana, polarització, recuperació, osmosi inversa.

SUSTAINABLE DEVELOPMENT GOALS

Water is the essence of life for all living beings. Although the oceans represent 97% of the water on the planet, it contains an average salinity of 3.5% by 100 g of seawater, and it is not suitable for human consumption. This arouses great interest in freshwater. However, modern development and mismanagement of hybrid resources have a great impact on water quality, causing diseases. Therefore, water pollution is a problem on a global scale [1], [2].

Most water pollutants remain dissolved or suspended chemicals in the water, thus affecting the physicochemical properties of the water and harming the environment. Pollutants are formed due to a physical, chemical, or biological factor[1].

However, the main concern is livestock farming and the excessive use of fertilizer for crops. In recent years, slurry farming has grown in Spain. This mixture has a high nitrogen content and when it is disposed in nature, especially in the form of urea, it seeps into the soil and can end up contaminating aquifers. Most of the urea is made up of ammonium. In this context, the Nitrates Directive established a Code of Good Agricultural Practice (CBPA) regarding the use of nitrogen, as well as the reduction of nitrogen content in nutrients and the use of treated slurry excrements for fertilizer [3].

On the other hand, the requirement for water purity is increasing, both for human consumption and for many industries. Thus, reverse osmosis membrane technology is one of the existing potential alternatives to purify water, despite the demanding energy requirements. In this situation, the need is created to optimize the plant to lower the energy cost.

The equipment which has the major impact in terms of energy consumption in the reverse osmosis system is the pump. These can be differentiated between low pressure, to drive the water to the plant, and high pressure, to drive the water through the membrane. In the first case, energy consumption is highly dependent on the distance of water collection, thus a good design of the plant location can reduce these costs. However, high pressure pumps depend on the membrane structure and salt concentration, and generally requires more power than the lower pressure

pumps [4]. Typically, seawater requires a pressure between 65 and 70 bar, whereas brackish water will require less pressure [5].

For this reason, it is interesting to recover energy by taking advantage of the pressure of the process, reducing the overall consumption of the plant. Initially, inverter pumps were used, driven by the pressure and flow of the brine, but soon Pelton turbines were introduced with the aim of obtaining higher recovery performance. Nowadays, turbocharged have become popular since of their higher performance than the previous ones. These operate as a double stage system, which the brine still under pressure from the first stage is fed to the second stage of membranes. This system is not necessary to incorporate recirculation [5][6].

Another possibility is to design a more durable membrane. Extending the life of the membrane leads to lower replacement costs and a reduction in the amount of used membranes that are discarded. The TFC membranes are typically used in reverse osmosis because of their strength and durability. This type of membrane consists of three layers: a polyester backing strip, a microporous polysulfide interlayer and an ultra-thin barrier coating on the upstream Surface [3]. However, other polymeric membrane alternatives, such as zeolite membranes for the treatment of various types of water [2].

1. REVERSE OSMOSIS

In recent decades, membrane technology has become a fundamental part of water treatment, such as ground, surface, waste and even salt water. It is economical because it has low energy costs and does not require the addition of chemicals [7].

General terms, a membrane is defined as an interfacial structure that separates two phases and acts as a selective barrier to transport of matter, thus restricting the movement of some species while allowing other species to permeate through it (crossing from one phase to another). To transport of matter across the membrane is due to the action of a driving force. Depending on the type of membrane separation process, it can be electric potential gradient, concentration gradient, or pressure gradient. Normally, membrane is classified according to their nature and morphology (size, microstructure, and macrostructure) [6], [7].

Thus, reverse osmosis technology can be defined as a unitary separation operation using a semipermeable membrane within its module, whose driving force is a pressure gradient. Unlike other separation processes with the same driving force (such as nanofiltration, ultrafiltration and microfiltration), reverse osmosis has the particularity that smaller particles can be separated (ionic range)[6].

This Chapter will explain the generalities of reverse osmosis, the overview of the process and polarization with the models that will be used in the proposed experiments.

1.1. GENERALITIES OF REVERSE OSMOSIS

If two aqueous salt solutions of different concentrations are separate by a semipermeable membrane, which is permeable to the solvent (water) and impermeable to the solute (salt), the solvent from the more concentrated solute solution (phase 1) will move to the less concentrated solution (phase 2). This phenomenon is known as reverse osmosis [8], [9].

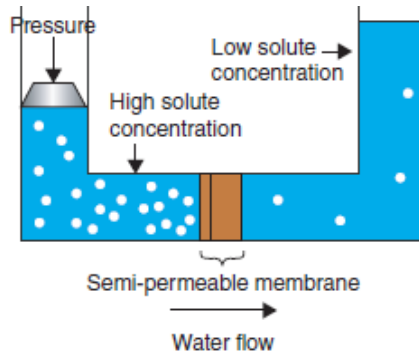


Figure 1. Schematic view of reverse osmosis phenomenon.

This happens when the two phases are at different hydrostatic pressures since phase 2 applies an external pressure higher than the osmotic pressure. Therefore, it is important to know the osmotic pressure of the salt for the solvent to pass through the membrane[8].

According to Van't Hoff, there is a relationship between the ideal gas laws with dilute solutions [9]. Thus, he deduced that the osmotic pressure equation is:

$$\pi = iCRT \quad \text{eq. (1)}$$

where π is the osmotic pressure, i the number of chemical species involved in the system, C the solute concentration, R the gas constant and T the temperature.

Depending on the structure of the membrane, porous or non-porous, two types of models can be distinguished to describe the transport of fluid across the membrane: porous flow and solution-diffusion [7], [10].

Porous flow models consider the active layer of the membrane to be a porous structure and give rise to diffusion and convection. In contrast, solution-diffusion models assume that

the active layer of the membrane is made of a non-porous material and only diffusion is involved[11].

Reverse osmosis membranes are commonly non-porous. However, the term non-porous refers to those pores at the molecular level that allow transport across the membrane. Basically, transport across the membrane can be expressed as a function of fluid permeability [10].

$$P = S \times D \quad \text{eq. (2)}$$

where P is the permeability of the fluid passing through the membrane, S the solubility which indicates the amount of penetrant sorbed by the membrane under equilibrium conditions, and D the diffusivity which measures the rate of penetration transported across the membrane [10].

Thus, the diffusivity can be determined by the expression of Fick's law:

$$J = -D \frac{\Delta C}{\Delta x} \quad \text{eq. (3)}$$

where J is the flux through the membrane, ΔC is the concentration gradient and Δx is the distance gradient.

In industrial processes, membranes are packaged into modules to provide better performance[6]. Modules are defined as a housing with a specific geometry that completely covers the membrane, with a feed inlet and two outlets, the concentrate and the permeate. The reverse osmosis modules can be made of spiral wound, hollow fiber, tubular, and plate and frame formats[6]. However, spiral wound modules are generally used in the reverse osmosis industry. These are more economical because these occupy less volume in the plant for the same performance.

The most used reverse osmosis membrane applications are synthetic in nature, namely thin film composites (TFC). These are materials resistant to high temperatures and different chemicals [11], since the TFC membranes are made of aromatic polyamides[6]. The structure of this membrane has the particularity of having an ultrathin PA film (10 – 1000nm) and a porous support layer. The ultrathin film serves to make the membrane selective, while the support layer acts as an enhancer of the mechanical strength of the membrane [11].

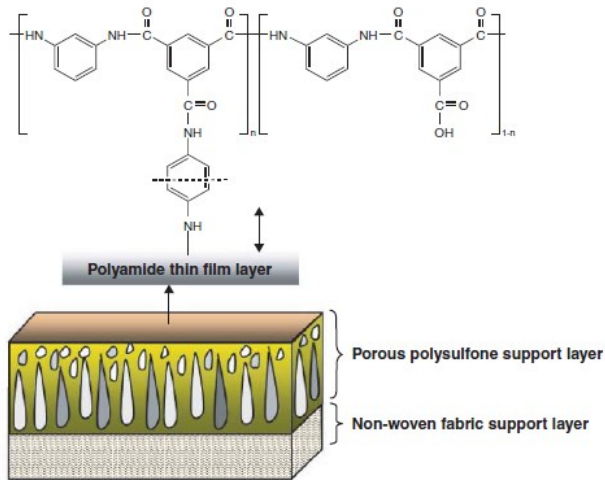


Figure 2. Schematic view of TFC and the chemical structure of aromatic polyamide.

Furthermore, the membrane can be Brackish Water (BW) or Seawater (SW). The difference between one and the other is as the name indicates. The BW for low concentrations of salt, coming from groundwater, wastewater, and surface water. In contrast, SW for high concentrations of salts from seas. Normally, the BW membrane retains 98.5% NaCl and the SW 99.5%. However, this is quite dependent on the membrane manufacturer.

Reverse osmosis serves mainly for the desalination of water, which are used for human consumption. However, obtaining certain water purity standards is needed more in industrial processes [4], as well as:

- Pharmaceutical industries for the creation of pharmaceutical products require the use of very pure water free of dissolved particles, bacteria, and organic debris.
- The sanitary industries use pure water as raw material for laboratory techniques and analysis instrumentation. Also, for the thermal sterilization and disinfection of sanitary instruments and medical equipment.
- The food and beverage industry since it is often a component of the product. In addition, the pure water is also used for refrigeration, steam production and cleaning.
- Among other industries that require the use of high purity water.

1.2. OVERVIEW OF THE PROCESS

The principle of reverse osmosis is based on forcing a solvent through the membrane and retaining salts, under the gradient of the pressure difference as the driving force[10].

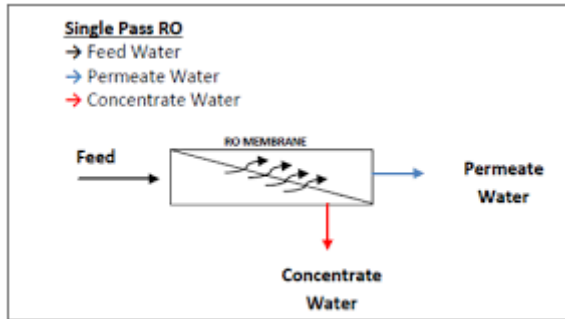


Figure 3. Simple diagram of reverse osmosis process.

In the process, the feed enters the module to contact the surface of the semipermeable membrane. Some components permeate through the membrane and exit through the permeate stream, while others are retained in the reject stream. To carry out this separation, it is necessary to apply a pressure higher than the osmotic pressure of the salt in the reject stream [8].

The performance of the process is related to the flow rate of the outlet streams and the properties of the membrane. Thus, its performance can be assessed by the observed rejection equation:

$$R_{\text{obs}} = 1 - \frac{C_p}{C_R} \quad (\text{eq.4})$$

where C_p is the permeate concentration and C_R is the rejection concentration.

Being a non-porous membrane, the transport of the flux through the membrane is mathematically part of the solution-diffusion model [10]. Thus, the solvent flux is given by the following equation:

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \quad (\text{eq.5})$$

where L_p is the water permeability, ΔP is the transmembrane pressure gradient, σ is the reflection coefficient and $\Delta\pi$ is the osmotic gradient.

The relationship between the solute permeability through the membrane and the solute retention on the membrane, can be estimated by the reflection coefficient (σ). If σ is 1, the solute does not permeate and is retained on the membrane. But if σ is 0.50, it means that half of it permeates, since the solute is carried away by the solvent crossing the membrane, and the other half is retained.

In contrast, for the solute flux can be related to the permeate concentration and the solvent flux [12], giving the following equation:

$$J_s = C_p J_v \quad (\text{eq.6})$$

This equation can be rewritten in terms of the solute permeability and concentration gradient, achieving:

$$J_s = L_s \Delta C \quad (\text{eq.7})$$

The concentration gradient is the difference between the concentration of the rejection in the boundary layer and the permeate concentration at a given time [13]. With this, a concentration profile can be made, and the effect of polarization can be assessed.

However, the Spiegler-Kedem model proposes to determine the theoretical rejection without polarization related to the reflection coefficient, the solvent flux, and the permeability of the solute [12] ,[14]. The simplified equation is as follows:

$$R_t = \frac{\sigma(1-F)}{1-\sigma F} \quad (\text{eq.8})$$

where F is given by the following expression:

$$F = \exp \left[\frac{-(1-\sigma)}{L_s} J_v \right] \quad (\text{eq.9})$$

Rewriting equation (8), it follows that the solvent flux across the membrane is:

$$J_v = \frac{L_s}{1-\sigma} \ln \left(\frac{\sigma(1-R_t)}{\sigma-R_t} \right) \quad (\text{eq.10})$$

1.3. POLARIZATION CONCENTRATION

As the process proceeds, retained solutes accumulate on the membrane surface, causing a reduction of the solvent flux in the permeate. Therefore, worse salt recoveries. This is because solute back diffusion is much slower than feed convection. Thus, the solute concentration gradually increases near the membrane over time, forming a boundary layer near the membrane wall. This phenomenon is known as concentration polarization [15].

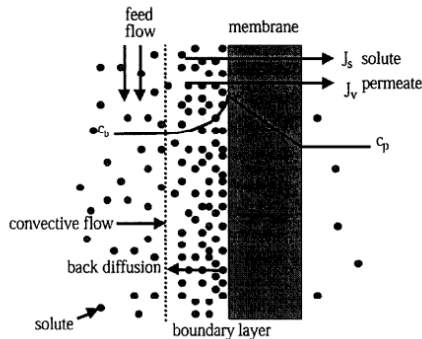


Figure 4. Schematic representation of concentration polarization.

In addition, polarization has other negative effects, such as [15]:

- Increased osmotic pressure near the membrane wall, with a consequent decrease of water flux in the membrane.
- Scaling or particles fouling in the case of accumulation of solutes on the membrane with a concentration higher than the solubility of the solutes, leading to a decrease in flux.
- Increase in the concentration gradient of solutes across the membrane, leading to increased solute flux and thus reduced solute rejection.
- Membrane deterioration due to fouling resulting from concentration.

To decrease the effect of polarization, it is recommended to [15]:

- Increase the rate of solute back-diffusion by increasing the temperature or by enclosing the feed stream in the boundary layer.
- Increase the crossflow velocity across the membrane.
- Add turbulence promoters, spacers, etc, to the membrane module.

The mass transfer coefficient of the solute plays an important role in deducing whether the polarization exists in the membrane. This coefficient indicates the ease of solute transfer in the membrane. Therefore, it is interesting that this coefficient is higher, so that the salts will not have enough time to deposit on the membrane surface as a barrier.

The polarization effect can be approximated in the following ranges:

- Little polarization: $k > 10^{-4} \text{m/s}$
- Moderate polarization: $10^{-4} \text{m/s} < k < 10^{-5} \text{m/s}$
- Much polarization: $k < 10^{-5} \text{m/s}$

There are several models that describe this phenomenon by empirical correlations of the mass transfer coefficient or experimental concentration profile estimates. In the following subsection, some of the models will be detailed.

1.3.1. Film model

This model consists of a profile concentration to estimate the thickness of the boundary layer caused by polarization. Likewise, the mass transfer coefficient of the solute can be determined in relation to the diffusivity and thickness.

The rejection of ionic species presents high salt concentrations near the surface of the local concentrated membrane, this layer quickly reaches steady state and the cross flow through the concentration polarization (CP) layer is constant [16]. Thus, the transfer balance that takes place across the membrane relates the flux to Fick's law, giving the following equation:

$$J_v \cdot C_p = J_v \cdot C - D \frac{dc}{dx} \quad (\text{eq.11})$$

where J_v is the solvent flux, C_p is the permeate solution concentration, C is the solute concentration in the boundary layer, and D is the solute diffusion coefficient.

Considering the distance that this concentration profile produces, from the membrane surface to a finite thickness of the film boundary layer [12], and integrating, the relationship between concentration polarization and permeate flux is obtained:

$$CP = \frac{C_m - C_p}{C_b - C_p} \quad (\text{eq.12})$$

where C_m is the concentration at the surface or channel wall for the rejected salt and C_b is the bulk solute concentration.

Thus, the latter equation can be expressed by relating the solvent permeate flux to the solute diffusivity and the boundary layer thickness (δ):

$$CP = \exp\left(\frac{J_v \delta}{D}\right) \quad (\text{eq.13})$$

The solute transfer coefficient can be expressed as a function of diffusivity and the boundary layer thickness:

$$k = \frac{D}{\delta} \quad (\text{eq.14})$$

Substituting the latter term in equation (13), it follows that CP can be related to the solvent permeate flux and the solute transfer coefficient:

$$CP = \exp\left(\frac{J_v}{k}\right) \quad (\text{eq.15})$$

1.3.2. Determination of the transfer coefficient using Sherwood model

The Sherwood model allows the generalization of mass transfer correlations as a function of fluid velocity both turbulent and laminar regimes. Thus, the Sherwood number relates the Reynolds number (Re), Schmidt number (Sc) and the flow geometry in the form [14], to the following equation:

$$Sh = a \cdot (Re)^\alpha \cdot (Sc)^\beta \left(\frac{d_h}{L}\right)^\gamma \quad (\text{eq.16})$$

Relating the velocity to the Reynolds and Schmidt to the diffusivity, the defined equation is obtained:

$$\frac{k d_h}{D} = a \cdot \left(\frac{\rho v d_h}{\mu} \right)^\alpha \cdot \left(\frac{\mu}{D} \right)^\beta \left(\frac{d_h}{L} \right)^\gamma \quad (\text{eq.17})$$

where k is coefficient of mass transfer, d_h is the hydraulic diameter, D is the solute diffusivity in water, ρ is the density, μ is the kinematic viscosity, v is the flow velocity and L is the length of the tube channel. The α , β and γ are constant parameters that are estimated in the literature, also the a that characterizes the flow channel geometry [14].

If the velocity is changing and all other properties are held constant, the mass transfer coefficient of the solute is obtained:

$$k = K \cdot v^\alpha \quad (\text{eq.18})$$

where K is the properties constant and normally α is 0.57[17].

Thus, the latter equation can be related to the Spiegler-Kedem model, as follows:

$$\ln \left(\frac{1 - R_{\text{obs}}}{R_{\text{obs}}} \right) = \ln \left(\frac{1 - R_t}{R_t} \right) + \frac{1}{K} \frac{J_v}{v^\alpha} \quad (\text{eq.19})$$

where R_{obs} is the observed recovery, R_t is the theoretical recovery and J_v is the solvent flux.

1.3.3. Combined Spiegler-Kedem/ film model

Combining the Spiegler-Kedem model with the film model, the solute transfer coefficient can be estimated [12].

In this case, the theoretical rejection with polarization according to the Spiegler-Kedem model:

$$R_t = \frac{\sigma(1-F)}{(1-\sigma) \exp\left(\frac{J_v}{k}\right) + \sigma(1-F)} \quad (\text{eq.20})$$

where the *exponential term* is given by the film model (equation 15) and F is the following expression:

$$F = \exp \left[\frac{-(1-\sigma)}{L_s} J_v \right] \quad (\text{eq.21})$$

Thus, rewriting equation (20) a linear regression of the model can be obtained:

$$\ln \left(\frac{1 - R_{\text{obs}}}{R_{\text{obs}}} \right) = \ln \left(\frac{1 - R_t}{R_t} \right) + \frac{J_v}{k} \quad (\text{eq.22})$$

2. OBJECTIVES

The main aim of this work is to evaluate the performance of a reverse osmosis membrane for the recovery of ammonium ions, a nutrient found in many effluents.

To achieve this main goal, the following objectives are proposed:

- Characterization of a reverse osmosis membrane with permeate flux and NaCl rejection.
- Quantify the influence of temperature on water permeability.
- Investigation of the permeation of ammonium and ammonia as a function of the concentration and the pH value of the starting solution.
- Determine the ammonia permeability by fitting the experimental results.

3. EXPERIMENTAL

3.1. MATERIALS AND CHEMICAL REAGENTS

This section is shown the materials and chemical reagents used during the experimentation.

The materials are as follows:

- Thermostatic bath and condenser
- Pump with frequency controller
- Sepa CFII flat module
- Brackish Water Reverse Osmosis Membrane (DuPont)
- Spacer (14 mil) and three stainless shims (25 + 15 + 10) mil
- Pressure valve, monometer, and thermometer
- Plastic container and feed glass container (2.5 L)
- Graduated Cylinder (1 L, 20 mL)
- Volumetric Pipette (2, 5, 10, 20) mL
- Volumetric Flask (2000, 500) mL
- Analytical Balance (precision ± 0.0001 g)
- pH-meter
- Conductivity meter
- High Performance Ammonia Ion Selective Electrode (Thermo Fisher Scientific)
- Chronometer
- Magnetic stirrer

However, the reactive are:

- Distilled Water
- Sodium Chloride
- Ammonia Chloride
- Ammonia Sulfate
- Sodium Hydroxide 0.1M
- Hydrochloric Acid 37%
- 1000 ppm ammonia as nitrogen standard for analysis.

3.2. INSTALLATION

The reverse osmosis system comprises the following elements: feed glass container, thermostatic bath, condenser, pump with frequency controlled, pressure valve, monometer, thermometer and, the most fundamentally, the reverse osmosis flat membrane module with its membrane, spacer, and stainless shims. All the system is connected by hoses with their corresponding diameters. Below, can see this system:



Figure 5. Reverse osmosis system.

As shown in the Figure 5, the feed container is submerged on the thermostatic bath, to determine the required temperature, and the condenser, to stabilize the temperature. To this

container offers two inlets, permeate and rejection, and one outlet, feed on account of the recirculation. The pump with frequency controller is connected at the outlet, so the fluid enters the reverse osmosis module. The module has two outlets which are the rejection and the permeate. The latter has a monometer and a pressure valve to regulate the working pressure of the system, which must be higher than the osmotic pressure of the salt used. Both rejection and permeate are returned to the feed container.

In addition, the module has a safety system to prevent the steel plates from being separated due to the working pressure exerted. Consequently, it is important to press it every time the experiments are performed.

The interior of the membrane module includes a membrane, stainless shims, and a plastic mesh for the fluid to circulate in turbulent regime minimizing polarization, known as spacers.

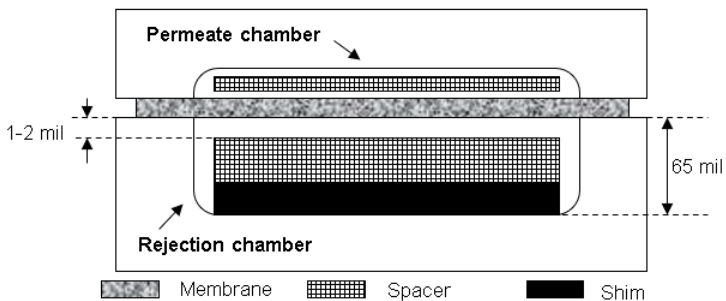


Figure 6. Schematic view of module interior.

The spacer and shims have different thicknesses. Therefore, the following configuration is proposed for this experiment:

Table 1. Shims configuration.

Inside the membrane module	Thickness [mil]
Spacer	14
Shim 1	25
Shim 2	15
Shim 3	10
Minimum rejection chamber depth	1
Total rejection chamber depth	65

3.3. PROCEDURE

3.3.1. Pump calibration

Initially, the pump is calibrated to determine the relation between the flow rate pumped and the pump frequency.

To proceed with the calibration, the distilled water is feed in a plastic container, which is connected to the pump by two hoses (one hose belongs to the pump inlet and the other to the outlet). The frequency of the pump is established by means of a frequency controller, and the pump operates at the frequency set point for a period of 15 min. Once the time has elapsed, the flow rate is measured by means of a graduated cylinder and a chronometer, and the same procedure is repeated at different frequencies.

3.3.2. Reverse osmosis membrane with distilled water

The aim of this experiment is to determine the effect of temperature on the permeate flow rate of the distilled water operating at different pressures.

The reverse osmosis system is installed as mentioned in section 3.2. *Installation* and it is verified that there are no fluid losses. Afterwards, 2.5 L of distilled water is added in a glass container, and it immersed in the thermostatic bath with a condenser, where the temperature set point is regulated as required. Before starting up the experiment, the feed, permeate and rejection passages are connected with hoses. Then, the pump is switched on and the flow rate and pressure are set as required to allow the fluid to circulate through the system in the desired conditions for a period of 15 min. Once the temperatures have stabilized, the permeate flow rate is measured with the graduated cylinder and reintroduced into the feed container. In the following experiments inlet pressure is changed, up to six different working pressures for the three different target temperatures of the thermostatic bath.

3.3.3. Reverse osmosis membrane with synthetic water

In the case of synthetic water, a solution of 2.5 L of distilled water is prepared with a certain concentration of a known salt (see the 3.4. *Experimental Proposal* section to visualize the compounds and concentrations used). Depending on the study to be carried out, there are small changes when performing the experiment.

The effect of temperature

The same procedure is carried out as in the previous section of the distilled water but leaving the fluid to circulate for 45 min so that the system is in stationary regime. The flow rate is measured by collecting 20 mL of the permeate and the rejection in different vials, where it is also measured their conductivities and pH.

When synthetic water composed of NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ is used, a drop of concentrated HCl is added to the permeate vial, capped, and stored for ammonia analysis. The same procedure occurs with the first rejection vial each time the experiment is started. Whereas the latter rejections of these compounds as well as the permeate and the rejection of the synthetic water composed of NaCl are disposed. In these experiments, the working pressures chosen higher than the osmotic pressure of the salt.

When working at pH different from neutral, NaOH is added to the feed container to basify the system (see next paragraph).

The effect of pH

The experiment is carried out for one temperature only. It is worth mentioning that, before waiting the 45 min for basic media, it is necessary to ensure that the pH is not altered. Since the membrane acidifies the system when the fluid circulates being subjected to a pressure higher than the osmotic pressure. For this reason, the pH is expected to stabilize once temperature is stabilized first, but if it is altered, more drops of NaOH are added.

The effect of polarization at different frequencies

In this case, the pressure is maintained constant. In this sense, instead of changing the pressure each time it is waited 45 min to reach the steady state, the pump frequency is changed.

Membrane cleaning

It is essential to wash the membrane when the component is changed and/or if different concentrations are made for the same component. To do this, the contents of the feed container disposed of and washed with distilled water. The feed container is filled with distilled water, immersed in the thermostatic bath without turning it on and the three hoses are inserted. The pump is turned on at frequency 8, the pressure valve is fully opened, the monometer is adjusted (minimum over 5 bar) and the water is allowed to circulate for 20 min. Once this time has elapsed, the monometer is lowered to 0 bar, the pressure valve is completely closed, the pump frequency is gradually lowered to the 0 and the pump is switched off. The contents of the container are poured into the sink and the same procedure is repeated a second time.

3.3.4. Ammonia analysis

The ammonia analysis consists of evaluating the ammonia concentration of the stored permeate and rejection vials for the compounds NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$, mostly in basic media (plus ammonia formation).

Total Ammoniacal nitrogen concentration was determined using a Thermo Fisher Scientific selective electrode (Orion 9512HPBNWP) following the procedure 4500-NH3D and a calibration curve with standard solutions of different total ammoniacal nitrogen concentrations.

3.4. EXPERIMENTAL PROPOSALS

First, the membrane performance was characterized by the permeation of pure water and NaCl solutions at different temperatures, as the typical procedure found in literature. It is known that reverse osmosis membranes have a characteristic NaCl rejection. Later, the permeation of ammonia was evaluated at different initial conditions. All the experiments conducted are shown in Table 1.

Table 2. Proposed experimental conditions.

Solute	T [°C]	Feed pH	Feed solute concentration [M]	Frequency [Hz]
Water	20, 25, 30	-	-	8
NaCl	20, 25, 30	7	0.1	8
		10.5	0.1	6, 8, 10, 11
NH ₄ Cl	20, 25, 30	7	0.1	8
	25	7, 9.5, 10.5, 11.5	0.1, 0.15, 0.20, 0.25	8
(NH ₄) ₂ SO ₄	25	7, 10.5, 11.5	0.05	8

The module of the membrane is flat geometry, Sepa CFII, since it is easier to perform the study.

The choice of membrane is Brackish Water Reverse Osmosis Membrane due to working with low salt concentrations. This membrane is a polyamide thin film composite and non-porous. In the following table shows the operating and cleaning limits for this membrane.

Table 3. Operating and cleaning limits characteristics of the BW membrane.

Maximum Operating Temperature	113°F (45°C)
Maximum Operating Pressure	600psig (41 bar)
Maximum Element Pressure Drop	15psig (1.0 bar)
pH Range, Continuous Operation	2 – 11
pH Range, Short-Term Cleaning (30 min.)	1 – 13
Maximum Feed Silt Density Index (SDI)	SDI 5
Free Chlorine Tolerance	< 0.1ppm

Normally, it is studied at three pressures higher than the osmotic pressure of the salt to be used, although it must not exceed the maximum working pressure of the membrane.

4. RESULTS AND DISCUSSION

Experimental data were obtained from permeate and reject conductivities to achieve the salt rejection under certain working conditions, except for pure water since it does not contain dissolved solutes.

Likewise, the permeation time in a volume of 20 mL is obtained to calculate the permeate flow rate and thus the permeate water flux through the membrane having an area of 1.378 cm².

By means of the analysis with the ammonia selective ion electrode, the concentrations of N-NH₃ in the permeate and the rejection of NH₄Cl and (NH₄)₂SO₄ are acquired to evaluate the retention of this solute.

4.1. PURE WATER

4.1.1. The effect of temperature

Regarding on the applied working pressure, the permeate water flux through the membrane is proportional to the transmembrane pressure. As the pressure increases, the flow that across the membrane will also be higher. This correlation is also influenced by temperature, as it can be seen in the following Figure 7.

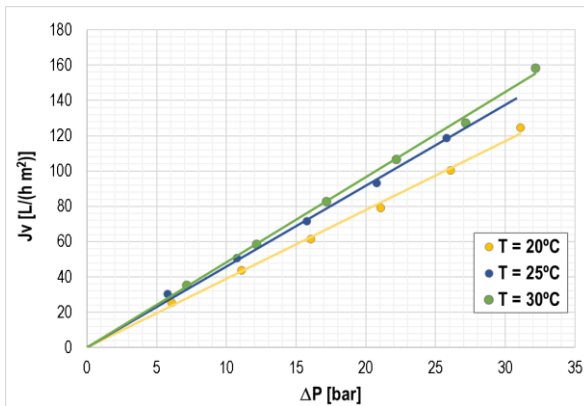


Figure 7. Correlation of permeate pure water flux with different temperatures.

This ratio is described by the equation (5) and is reflected in the following table:

Table 4. Solvent flow through the membrane at different temperatures.

T [°C]	$J_v = L_p (\Delta P - \sigma \Delta \pi)$
20	$J_v = 3.902 \Delta P$
25	$J_v = 4.586 \Delta P$
30	$J_v = 4.831 \Delta P$

The slope belongs to the permeability of pure water in units $L / (h \cdot m^2)$ at each temperature and the origin of ordinates is 0, because pure water has not osmotic pressure since it contains not dissolved solutes.

Therefore, the values of water permeability are affected with temperature, it is observed that there is an Arrhenius relationship as seen in the Figure 8.

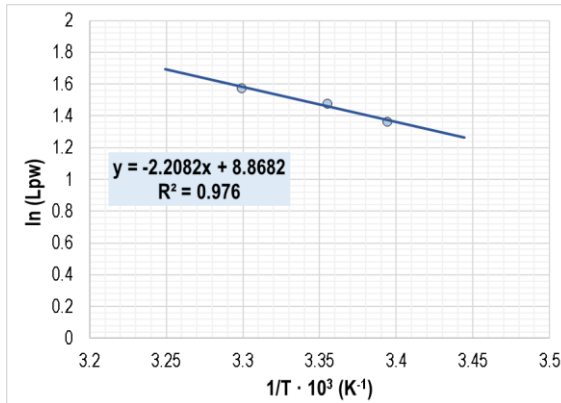


Figure 8. Effect of temperature on water permeability.

Increasing the temperature leads to higher water permeability, since its viscosity decreases and its fluidity increases. Thus, the transport of the solvent across the membrane by diffusion will be higher rapidly.

4.2. SODIUM CHLORIDE

4.2.1. The effect of temperature and pH

Sodium Chloride is the reference salt, since considered as it is the common salt and one of those responsible for water salinity. For this reason, it is popular to characterize the membrane with this solute.

Theoretically, this membrane has a NaCl rejection of 98.5% since the membrane used is BW for fresh water (salt concentrations lower). In Figure 9, the neutral and basic pH rejections at different temperatures of 0.1M NaCl as a function of transmembrane pressure are plotted.

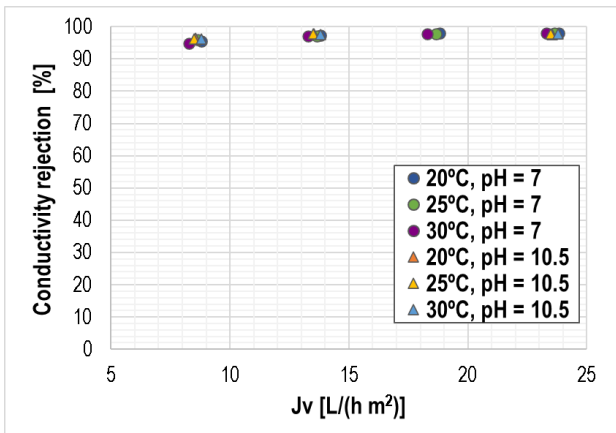


Figure 9. 0.1M NaCl rejection at neutral and basic pH with different temperatures.

The membrane pressure increases lead to a decrease in permeate conductivity and thus favours NaCl retention in all cases. The effect of temperature for the same pH shows an improvement in salt rejection when working at 25°C, because the membrane is sensitive to temperature. As for the effect of pH, there is a slight decrease in salts rejections for basic media since there are more ions to be separated (OH⁻).

In general, the salt rejection for all experiments is slightly below the theoretical value. In this way, the membrane can be considered to have retained the salts quite well.

Table 5. 0.1M NaCl rejection at a working pressure of 20 bar with different temperatures.

T [°C]	Neutral pH rejection [%]	Basic pH rejection [%]
20	98.11	97.57
25	98.11	97.85
30	97.93	97.74

Plotting the permeate water flux through the membrane as a function of transmembrane pressure as shown in Figure 10, it is observed that the permeate water flux is not affected by pH, except in the case of 20°C because it was worked at 1°C difference between neutral and basic pH. With respect to temperature, the slope is steeper as the temperature increases given that the permeability of the water increase.

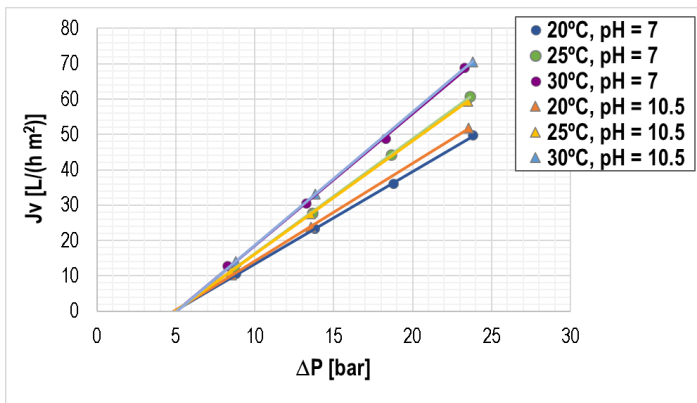


Figure 10. Correlation of permeate water flux with different temperatures and pH.

In all cases, about 5 bar is the osmotic pressure for NaCl at these conditions and, thus, the pressure that needs to be exceeded to carry out the separation of the salts. In fact, this value differs a little because the osmotic pressure in this experiment depends on the temperature as described by the equation (1), but it is not so sensitive.

The relationship between permeate water flux and transmembrane pressure is described by the equation (5) and is reflected in the following table:

Table 6. Solvent flow through the membrane at medium pH and 10.5 with different temperatures.

Feed pH	T [°C]	$J_v = L_p(\Delta P - \sigma\Delta\pi)$
7	20	$J_v = 2.612\Delta P - 12.70$
	25	$J_v = 3.240\Delta P - 16.03$
	30	$J_v = 3.733\Delta P - 18.74$
10.5	20	$J_v = 2.770\Delta P - 13.53$
	25	$J_v = 3.207\Delta P - 15.92$
	30	$J_v = 3.765\Delta P - 18.97$

The slope belongs to the water permeability in units $L / (h \cdot m^2)$ of each temperature with their respective pH and the origin of ordinates is different from 0 because there is an osmotic gradient of NaCl.

The values of water permeability are similar between neutral and basic media when compared at the same temperature, but it varies at different temperatures. In this sense, the water permeability is affected by the temperature and, accordingly, follows the Arrhenius equation as shown in Figure 11.

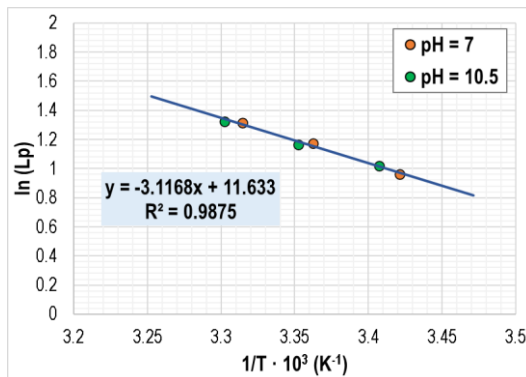


Figure 11. Effect of temperature on water permeability with different pH.

By estimating the permeability of the solute in neutral media at 25°C using equation (22), it is obtained that the permeability of 0.1M NaCl at these conditions is $8.331 \cdot 10^{-8}$ m/s for a σ of 0.98.

The σ is the maximum experimental rejection, and it is taken as a reference to these conditions to evaluate if it follows the same trend for the other experiments, as demonstrated in Figure 12.

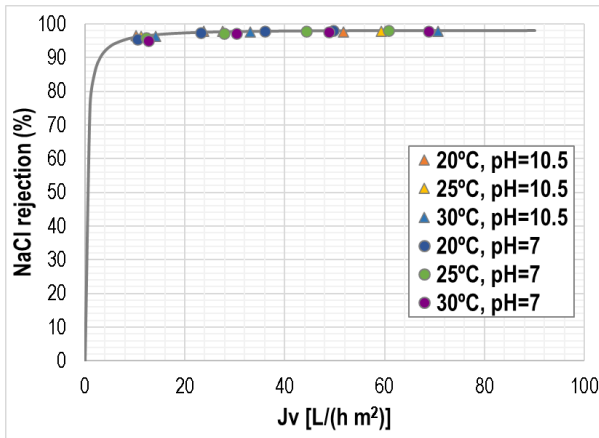


Figure 12. Correlation of NaCl permeability.

At neutral media the NaCl rejection tends to 98% which is the maximum salt retention for this experiment. However, this tendency is slightly lower for a basic media, so more dissolved ions must be separated, and it is reasonable that more flow rate is needed to increase the recoveries.

4.2.2. Polarization

It is important to know whether the solutes involved in the system cause the polarization effect. This phenomenon unleashes a barrier of solutes that are deposited on the membrane surface, making it impossible to filter pure water and, therefore, less rejection of salts.

The study consists of evaluating the polarization effect of 0.1M NaCl at pH 10.5 operating at 25°C and 20bar with different frequencies. The following table shows the salt rejection at these conditions:

Table 7.0.1M NaCl rejection at pH 10.5 with different frequencies.

Frequency	Salt rejection [%]
11	88.72
10	88.87
8	88.10
6	87.12

The pump frequency increases imply higher flow velocity and turbulence and, thus, favours salt retention. In this setting, the solutes do not have enough time to deposit on the membrane surface acting as a barrier. So, the flow velocity plays a very important role in the moment it traverses the membrane.

The velocities are obtained by the permeate water flux crossing the membrane spacer and the minimum depth in the rejection chamber, having a section of 0.038mm². According to the Spiegler-Kedem model, the mass transfer coefficient as a function of rate can be estimated by equation (19), where the observed rejection belongs to the experimental salt rejection and α is a theoretical parameter ($\alpha = 0.57$). In Figure 13, such model is represented for 0.1M NaCl in basic media.

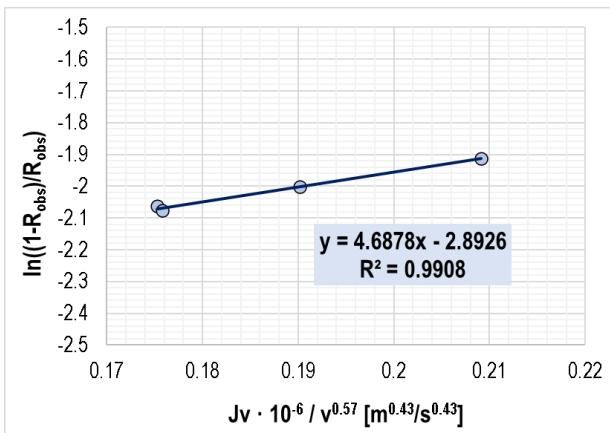


Figure 13. Correlation of Spiegler-Kedem model.

The origin of ordinates is the Napierian logarithm term of the theoretical rejection, resulting in a R_t of 94.75%. The slope belongs to the inverse of the constant used from the Sherwood number equation (17) which, in turn, gives the mass transfer coefficient of NaCl as a function of velocity related to equation (18) as shown in the following table:

Table 8. NaCl transfer coefficient as a function of velocity.

$k \cdot 10^5$ [m/s]	v [m/s]
2.288	1.130
2.167	1.028
1.908	0.822
1.620	0.617

As the velocity increases, the coefficient increases, because the mass of the solute is transferred more easily and rapidly to the membrane and therein its polarization decreases. In Figure 14, it is verified that the mass transfer coefficient is proportional to its velocity.

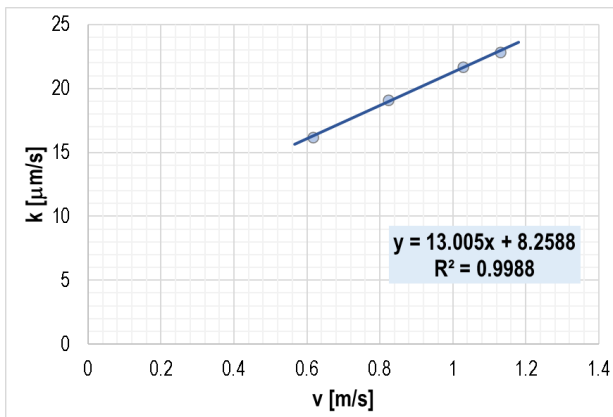


Figure 14. Correlation transfer coefficient 0.1M NaCl in basic media.

4.3. AMMONIUM CHLORIDE

4.3.1. The effect of temperature

To evaluate the effect of temperature for 0.1M NH_4Cl in neutral media, the higher the temperature implies an increase in permeate conductivity as the permeate water flux rate increases, as shown in Figure 15. However, it is observed that there is an operating point for all temperatures where the conductivity is maximum, so higher salt retention.

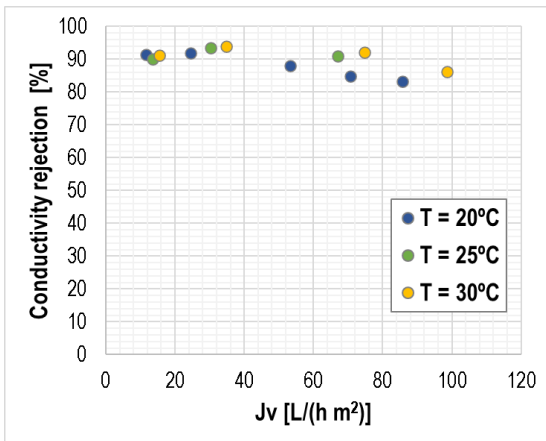


Figure 15. 0.1M NH_4Cl rejection in neutral media with different temperatures.

In this case, the working pressure is 10bar to obtain the best salt rejection, as seen in the following table:

Table 9. 0.1M NH_4Cl rejection at a working pressure of 10bar with different temperatures.

T [°C]	Salt rejection [%]
20	91.95
25	93.49
30	93.93

In general, the membrane can be considered to have retained the salts well under these conditions, since the rejection values are high but are lower when compared to NaCl. This is because the NaCl has a smaller ionic radius than NH₄Cl. Therefore, it will be easier for NaCl to pass through the membrane.

Plotting the permeate water flux as a function of transmembrane pressure as reflected in Figure 16, it appears that water permeability is higher with increasing temperature.

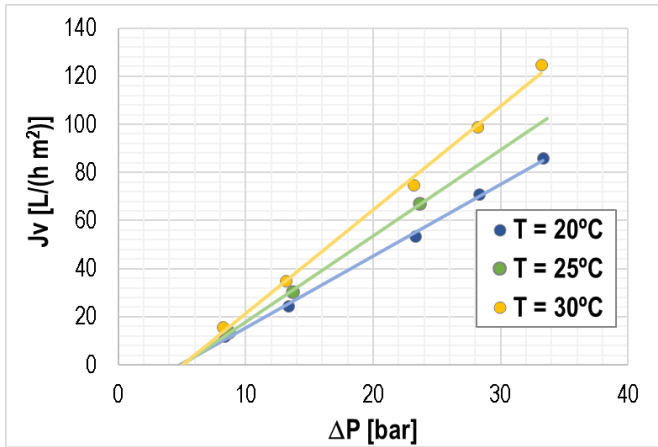


Figure 16. Correlation of permeate water flux with different temperatures.

In all cases, it is appreciated that NH₄Cl has the same osmotic pressure as NaCl, since the two salts are formed by two chemical species, have the same concentration and temperatures.

The relationship between permeate water flux and transmembrane pressure is shown in the following table, where the slope is the water permeability at each temperature and the origin of ordinates is different from 0 so there is an osmotic gradient of NH₄Cl:

Table 10. Solvent flow through the membrane at medium pH with different temperatures.

T [°C]	$J_v = L_p (\Delta P - \sigma \Delta \pi)$
20	$J_v = 2.984 \Delta P - 14.57$
25	$J_v = 3.577 \Delta P - 17.76$
30	$J_v = 4.307 \Delta P - 21.71$

The values of water permeability are affected by temperature, and hence, follow the Arrhenius equation as demonstrated in Figure 17.

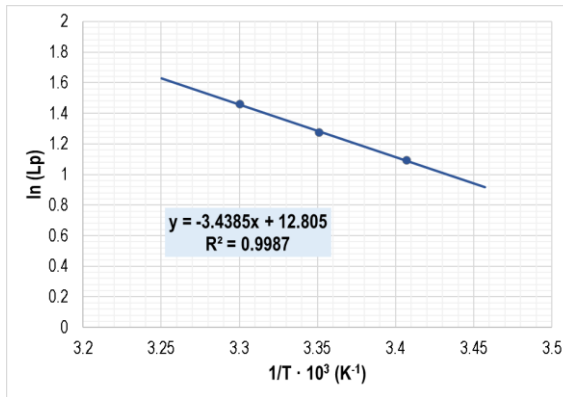


Figure 17. Effect of temperature on water permeability in neutral media.

Since the N-NH₃ permeability in neutral media is of interest, it is necessary to know the rejections of N-NH₃ by means of the concentrations resulting from the analysis. The following table, as shown these rejections at different working pressures:

Table 11. N-NH₃ rejection in neutral media with different temperatures.

ΔP [bar]	N-NH ₃ rejection [%]		
	T = 20°C	T = 25°C	T = 30°C
5	95.70	95.83	94.62
10	94.87	96.92	96.40
20	92.62	95.14	96.10
25	91.03	-	92.49
30	89.82	-	85.41

Generally, it favours the N-NH₃ rejection at low pressures, because increasing the working pressures implies worse retention of this salt. On the other hand, it is observed that it has a rejection of almost 97% at 10bar when working at room temperature.

By simulating the solute permeability of interest in neutral media using equation (22), the N-NH₃ permeability is obtained for different temperatures as seen in Table 12, where $\sigma \geq 0.97$ because it is the maximum experimental rejection, and all other temperatures are considered to have that parameter.

Table 12. Estimation of N-NH₃ permeability with reflection coefficient.

T [°C]	Ls·10 ⁸ [m/s]	σ [-]
20	6.327	0.97
25	8.306	0.97
30	12.58	0.98

Increasing the temperature leads to higher permeability of the solute as its viscosity decreases and, consequently, its fluidity increases.

When plotting the N-NH₃ rejections as a function of the permeate water flux as reflected in Figure 18, it is observed that as the flux increases, there is a decrease in the rejections on account of the membrane retains less N-NH₃ due to its polarization.

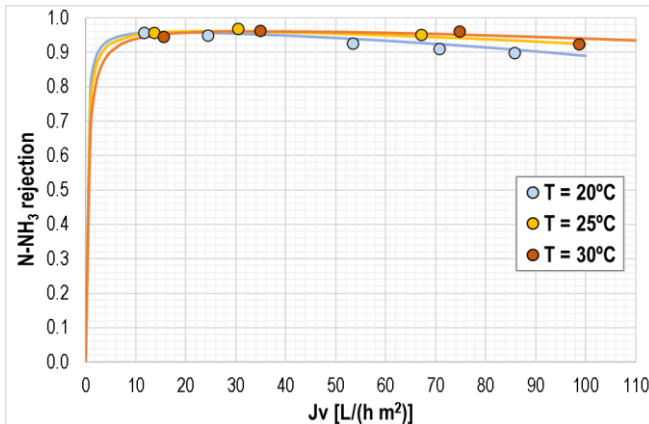


Figure 18. Correlation of N-NH₃ permeability with different temperatures.

4.3.2. Polarization at different temperatures

To assess the polarization effect of 0.1M NH_4Cl , the mass transfer coefficient of this salt is determined based on experimental data at different frequencies at pH 10.5 operating at 20 bar and 25°C using the Spiegler-Kedem model. As the NH_4Cl coefficient is of interest, the N- NH_3 rejections resulting from the analysis are used to calculate R_{obs} . Likewise, the frequency 8 is taken as a reference since the experiment to evaluate the effect of temperature was carried out at this frequency. In this case, the N- NH_3 rejection is 27.65% for a k of 2.321E^{-5} m/s, which is moderate polarization within the criteria.

Having a slight idea of the value of coefficient at these conditions, it is simulated for the different temperatures and in neutral media as a function of the N- NH_3 permeability obtained in Section 4.3.3. *Polarization*, as seen in Figure 19.

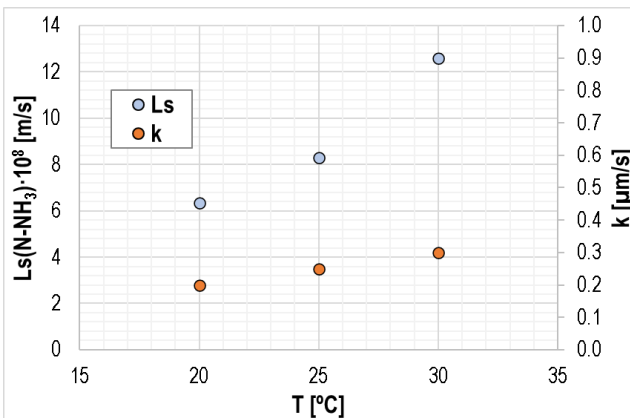


Figure 19. N- NH_3 permeability as a function of temperature and transfer coefficient.

The increase of temperature results in an increase of the mass transfer coefficient and, thus, polarization decreases. In this situation, the molecular diffusivity will be higher, since the solute movement velocity augments due to the temperature, and the thickness of the boundary layer will be lower, as described by equation (14). Therefore, the solute is transferred more easily and rapidly to the membrane and its polarization decreases.

In Table 13 shows the values of this simulation:

Table 13. Coefficient transfer 0.1M NH_4Cl in neutral medium at different temperatures.

T [°C]	$k \cdot 10^5$ [m/s]
20	2.011
25	2.491
30	3.023

However, all temperatures show moderate polarization according to the established criterion. Thus, a part of the solutes will be retained in the membrane forming a barrier to hinder the passage of the solvent, while the other part will be dragged by the flow through the membrane.

4.3.3. The effect of pH

To evaluate the effect of pH for 0.1M NH_4Cl from room temperature, there is an operating point where the rejection of salts is maximum. Consequently, the increase of the pressure at this point leads to a decrease in salt retentions, as shown in Figure 20.

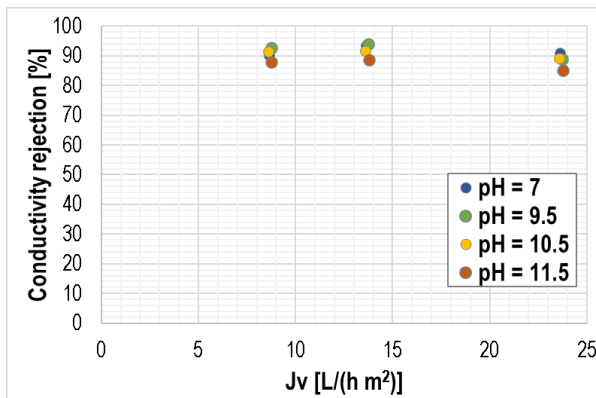


Figure 20. 0.1M NH_4Cl rejections with different temperatures.

In this case, the working pressure is 10bar to obtain the best salt rejection, as seen in the following table:

Table 14. 0.1M NH_4Cl rejection at a working pressure of 10bar with different pH.

pH	Salt rejection [%]
7	93.49
9.5	93.91
10.5	91.60
11.5	88.75

It should be mentioned that these rejections are due to the total salts of the system since it also forms NaCl in basic media. Generally, it can be considered that the membrane has retained the salts quite well under these conditions, as the rejection values are high. Likewise, it presents higher rejections at pH 9.5 than the others. However, it should give higher rejections at neutral pH because it does not have as many ions to separate and thus it is suspected that there is an experimental error.

Plotting the permeate water flux as a function of transmembrane pressure as demonstrated in Figure 21, the slope decreases at pH 11.5 since the permeability of water is low in contrast to the other media. This is because the water permeates less due to the complete formation of ammonia in the reaction and thus the water filtration rate decreases.

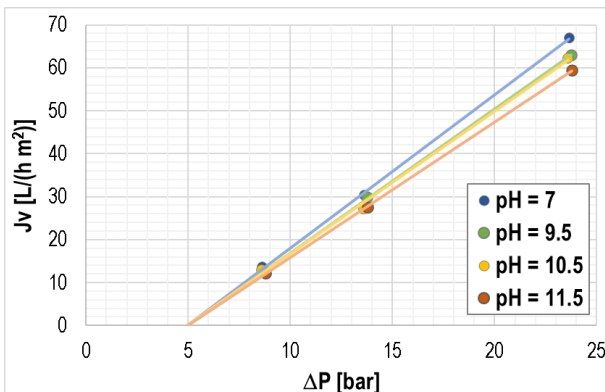


Figure 21. Correlation of permeate water flux with different pH.

In all cases, the osmotic pressure under these conditions is the same as in the previous section at 25°C, because the osmotic pressure does not affect the pH as described by equation (1).

The relationship between the permeate water flux with the transmembrane pressure is described by equation (5), where the slope belongs to the water permeability in units of each pH and the origin of ordinates is different from 0 owing to there is an osmotic gradient of NH₄Cl, as reflected in Table 15.

Table 15. Solvent flow through the membrane at medium pH with different pH.

pH	$J_v = L_p (\Delta P - \sigma \Delta \pi)$
7	$J_v = 3.577\Delta P - 17.76$
9.5	$J_v = 3.359\Delta P - 16.65$
10.5	$J_v = 3.313\Delta P - 16.43$
11.5	$J_v = 0.414\Delta P - 12.38$

As the N-NH₃ permeability at different pH is of interest, it is necessary to know the N-NH₃ recoveries by means of the concentrations resulting from the analysis. In the following table, rejections are shown at different working pressures:

Table 16. N-NH₃ rejection in neutral media with different pH.

ΔP [bar]	N-NH ₃ rejection [%]			
	pH = 7	pH = 9.5	pH = 10.5	pH = 11.5
5	95.83	95.23	56.17	32.81
10	96.92	79.04	54.85	32.81
20	95.14	81.04	51.91	33.38

In general, the better rejections are achieved in neutral media. As the pH alkalinity increases, it implies obtaining low retentions due to the presence of ammonia.

The estimation of the solute permeability at different pH using equation (22), it is simulated owing to the experimental rejections of N-NH₃ are relatively poor, because the ion selective electrode for ammonia in the analysis is very sensitive in determining its concentration. This simulation is given in the following table:

Table 17. Estimation of N-NH₃ permeability with reflection coefficient.

pH	$Ls \cdot 10^8$ [m/s]	σ [-]
07	8.312	0.98
9.5	42.90	0.92
10.5	113.1	0.67
11.5	170.1	0.53

Increasing the alkalinity of the media leads to higher permeability of N-NH₃. Therefore, lower rejections.

In Figure 22 represents the N-NH₃ rejections as a function of permeate water flux. It is observed that the trend drops at more basic media as the flux increases and hence lower N-NH₃ retention due to polarization. Thus, ammonia polarizes more than ammonium ion.

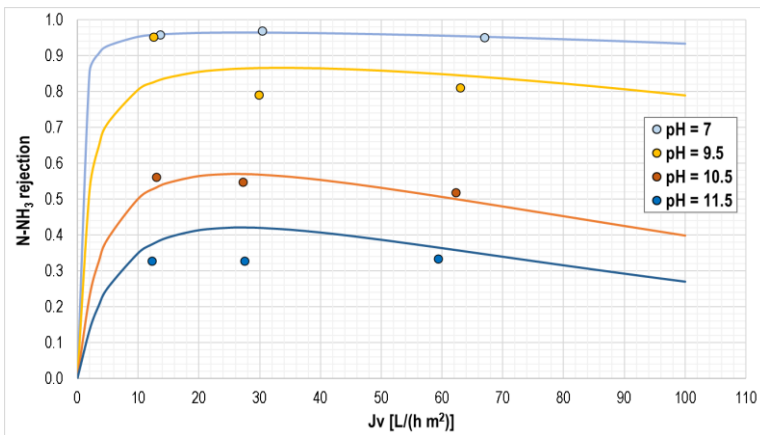


Figure 22. N-NH₃ rejections as a function of permeate water flux at different pH.

Plotting the N-NH_3 permeability at different pH with their respective σ as shown in Figure 23, increasing the alkalinity of the media implies a higher permeability of the solute. This is because it increases the concentration of ammonia on account of the shift of the equilibrium reaction favouring the formation of products due to the increase of OH^- concentration initially in the system, as described by Le Châtelier's principle. All NH_3 is formed at pH 11.5. In this context, the N-NH_3 retention is lower. Consequently, the water permeates less, making the filtration of pure water into the permeate impossible. However, N-NH_3 can be recovered in very basic media in the permeate.

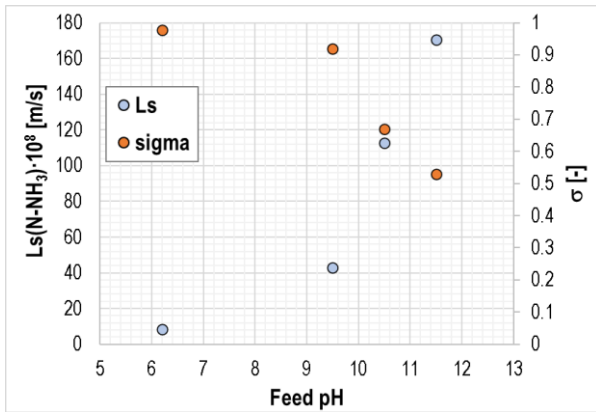


Figure 23. Permeability of N-NH_3 as a function of pH and σ .

4.3.4. The effect of concentrations and pH

After evaluating the effect of NH_4Cl concentrations in different media and comparing with the reference salt at 25°C , it is observed that NaCl has a higher rejection since it has a smaller ionic radius and thus it will be easier to cross the membrane. However, NH_4Cl concentrations are more affected as the alkalinity of the media increases as shown in Figure 24.

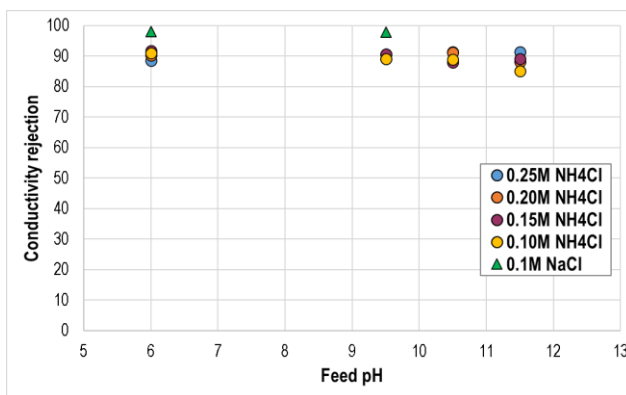


Figure 24. Rejection of NaCl and different concentrations of NH_4Cl .

When the NH_4Cl concentration is lower at pH 11.5, it implies worse retention compared to the other concentrations, since it polarizes at these conditions. For this reason, it is interesting to work with higher concentrations for this media. On the other hand, the rejection of the salt improves in neutral media when working with low concentrations.

Plotting the N-NH_3 rejection as a function of pH as seen in Figure 25, its rejection decreases as it completes the formation of the products in the reaction. Because the ammonia permeates through the membrane.

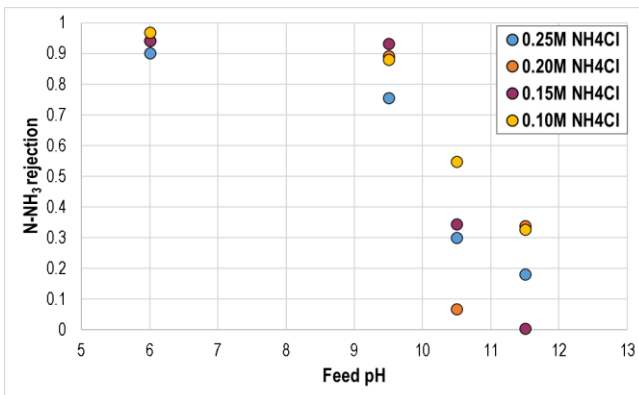


Figure 25. N-NH₃ rejection with different concentrations as a function of pH.

4.4. AMMONIUM SULFATE

4.4.1. The effect of pH

To evaluate the effect of pH for 0.05M $(\text{NH}_4)_2\text{SO}_4$, as the alkalinity of the media increases, there is a decrease in the conductivity of the permeate and the rejection of salts is not favoured, as shown in Figure 26. Nevertheless, it is observed that better retention of salts occurs when working at low pressures for all cases.

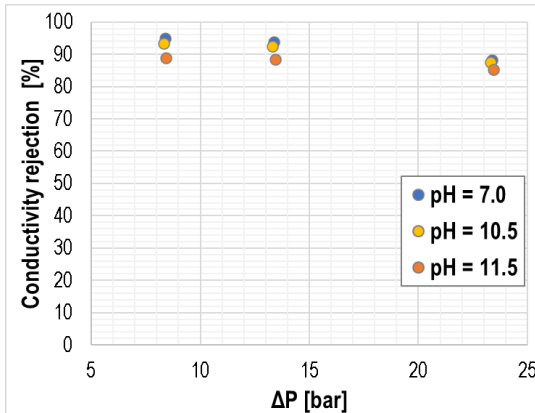


Figure 26. 0.05M $(\text{NH}_4)_2\text{SO}_4$ rejection with different pH.

In general, it can be considered that the membrane has retained the total salts quite well under these conditions because the rejection values are high, as seen in Table 18. Likewise, the rejections obtained are like NH_4Cl , but with different working pressures to achieve maximum retention.

Table 18. 0.05M $(\text{NH}_4)_2\text{SO}_4$ rejection at different pH and 5bar.

pH	Salt rejection [%]
7	94.98
10.5	93.51
11.5	88.96

Plotting the permeate water flux as a function of transmembrane pressure as demonstrated in Figure 27, the slope decreases at pH 11.5 since the permeability of water is low in contrast to the other media. This is because less water permeates due to the complete formation of ammonia. Consequently, the filtration rate of pure water reductions.

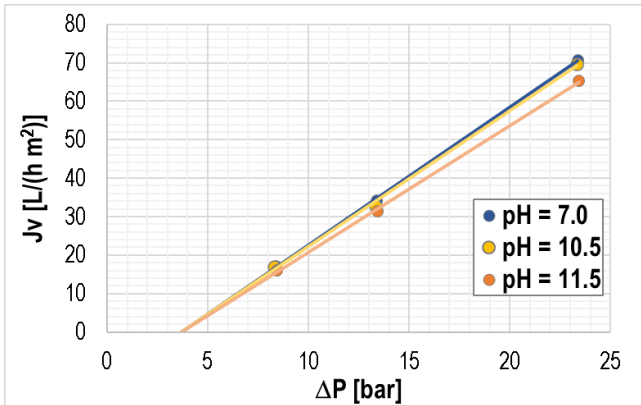


Figure 27. The water permeability as a function of the transmembrane pressure at different pH.

In all cases, it can be observed that about 4 bar is the osmotic pressure of $(\text{NH}_4)_2\text{SO}_4$ at these conditions and it is not affected by pH as mentioned in equation (1). Unlike the other two salts studied, $(\text{NH}_4)_2\text{SO}_4$ has less osmotic pressure owing to it has three chemical species.

The relationship between water permeate flux and transmembrane pressure is described by equation (5) and is reflected in the following table, where the slope belongs to the water permeability of each pH and the origin of ordinates is different from 0 because there is an osmotic gradient of $(\text{NH}_4)_2\text{SO}_4$.

Table 19. Solvent flow through the membrane with different pH.

pH	$J_v = L_p (\Delta P - \Delta \pi^w)$
7	$J_v = 3.584\Delta P - 13.33$
10.5	$J_v = 3.539\Delta P - 13.15$
11.5	$J_v = 0.414\Delta P - 12.38$

As the N-NH₃ permeability at different pH is of interest, it is necessary to know the N-NH₃ rejections by means of the concentrations resulting from the analysis. In the following table, rejections are shown at different working pressures.

Table 20. N-NH₃ rejection with different pH.

ΔP [bar]	N-NH ₃ rejection [%]		
	pH = 7	pH = 10.5	pH = 11.5
5	96.96	54.08	42.79
10	96.46	56.54	33.66
20	92.86	53.69	36.94

In general, it favours the N-NH₃ rejection for low pressures owing to increasing the working pressures leads to worse retention of this solute. On the other hand, it is observed that it presents better rejections in neutral media and that as the pH alkalinity increases, it implies obtaining low retentions due to the presence of ammonia.

The estimation of the solute permeability of interest at different pH using equation (X), it is simulated owing to the experimental rejections of N-NH₃ are relatively poor, since the ion selective electrode is sensitive. This simulation is given in the following table:

Table 21. Estimation of N-NH₃ permeability with reflection coefficient.

pH	$L_s \cdot 10^8$ [m/s]	σ [-]
7	8.312	0.98
10.5	113.1	0.69
11.5	170.1	0.55

Increasing the alkalinity of the media leads to higher permeability of N-NH₃ and, thus, lower solute rejection.

In Figure 28 shows the N-NH₃ rejections as a function of permeate water flux. At basic media, the trend drops as the flux increases and hence lower N-NH₃ retention due to polarization. Thus, ammonia polarizes more than ammonium ion.

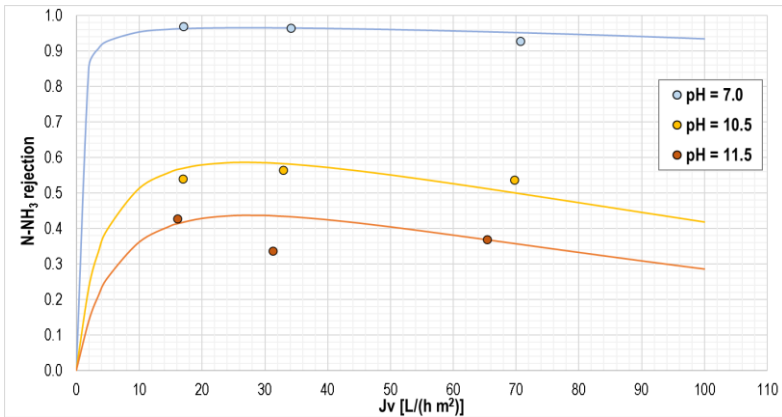


Figure 28. N-NH₃ rejection as a function of permeate water flux at different pH.

When representing the N-NH₃ permeability at different pH with their respective σ as seen in Figure 29, increasing the alkalinity of the media implies higher permeability of N-NH₃. This is due to increasing ammonia concentration since the reaction favours the formation of the products by increasing the OH⁻ concentration in the media. In this context, the retention of N-NH₃ is lower. Consequently, the water permeates less, and ammonia will be obtained in the permeate.

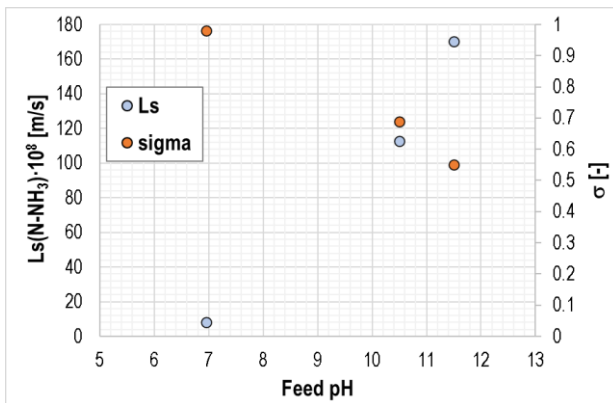


Figure 29. Permeability of N-NH₃ as a function of pH and σ .

N. CONCLUSIONS

The Brackish Water Reverse Osmosis Membrane is characterized by obtaining more purified water from fresh water.

For the characterization of the membrane, both water and solute permeability is influenced by temperature as it follows the Arrhenius equation. This is due increasing the temperature leads to a decrease in its viscosity, increases its fluidity and permeates more in the membrane. Also, implies better salt retention. On the other hand, as the alkalinity of the medium increases, it leads to a decrease in salt rejection since there are more ions to separate in the system. Likewise, the mass transfer coefficient of NaCl was evaluated to deduce if it presents polarization. In this case, a moderate polarization was obtained.

For ammonia nitrogen experiments, the N-NH₃ permeability also affects temperature by the Arrhenius equation. In addition, polarization decreases with increasing temperature since the solute transfer coefficient increases. Thus, the molecular diffusivity will be higher, and the boundary layer thickness will be lower. However, the polarization is moderate. On the other hand, at pH 11.5 all ammonia is formed. In this situation, the ammonia permeates more than the water and will go into the permeate. In contrast, the ammonium ion does not permeate the membrane and will go into the reject. Moreover, ammonia polarizes more than ammonium ion.

The reverse osmosis membrane at pH > 10.5 allows the recovery of ammonia nitrogen in the permeate.

REFERENCES AND NOTES

- [1] C. FN and M. MF, "Factors Affecting Water Pollution: A Review," *J Ecosyst Ecography*, vol. 07, no. 01, 2017, doi: 10.4172/2157-7625.1000225.
- [2] E. Nagy, "Reverse Osmosis," in *Basic Equations of Mass Transport Through a Membrane Layer*, Elsevier, 2019, pp. 497–503. doi: 10.1016/B978-0-12-813722-2.00020-0.
- [3] "01062017Responses_questionnaire_NAC_v4_final_final".
- [4] "Membrane_Handbook".
- [5] M. Di Martino, S. Avraamidou, J. Cook, and E. N. Pistikopoulos, "An optimization framework for the design of reverse osmosis desalination plants under food-energy-water nexus considerations," *Desalination*, vol. 503, May 2021, doi: 10.1016/j.desal.2021.114937.
- [6] Green, Don W, Southard, and Marylee Z, "Perry's Chemical Engineers' Handbook."
- [7] R. W. (Richard W. Baker, *Membrane technology and applications*. John Wiley & Sons, 2012.
- [8] "MEMBRANE_SEPARATION_PROCESSES".
- [9] "Química_aplicada_a_la_ingeniería".
- [10] M. Mulder, *Basic Principles of Membrane Technology*. Dordrecht: Springer Netherlands, 1991. doi: 10.1007/978-94-017-0835-7.
- [11] M. Zargar, B. Jin, and S. Dai, "Development and application of reverse osmosis for separation," in *Membrane Processes for Dairy Ingredient Separation*, Wiley Blackwell, 2015, pp. 139–175. doi: 10.1002/9781118590331.ch6.
- [12] T. Yaseen Khalaf Biomedical Engineering Dept, "Estimation of Concentration Polarization Using the Combined Film theory/ Spiegler-Kedem Model and Empirical Correlation," 2008.
- [13] D. Van Gauwbergen and J. Baeyens, "Separation uriiication Technology ELSEVIER Modelling reverse osmosis by irreversible thermodynamics," 1998.
- [14] T. Yaseen Khalaf Biomedical Dngineering Dept, "Estimation of Concentration Polarization Using the Combined Film theory/ Spiegler-Kedem Model and Empirical Correlation," 2008.
- [15] M. Zargar, B. Jin, and S. Dai, "Development and application of reverse osmosis for separation," in *Membrane Processes for Dairy Ingredient Separation*, Wiley Blackwell, 2015, pp. 139–175. doi: 10.1002/9781118590331.ch6.
- [16] C. Chen and H. Qin, "A mathematical modeling of the reverse osmosis concentration process of a glucose solution," *Processes*, vol. 7, no. 5, May 2019, doi: 10.3390/pr7050271.

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- [17] E. Dražević, K. Košutić, and V. Dananić, "Mass transfer of differently sized organic solutes at spacer covered and permeable nanofiltration wall," *Chemical Engineering Journal*, vol. 244, pp. 152–159, May 2014, doi: 10.1016/j.cej.2014.01.043.

APPENDICES

APPENDIX 1 PUMP CALIBRATION

The pump calibration in relation to the feed flow rate and pump frequency.

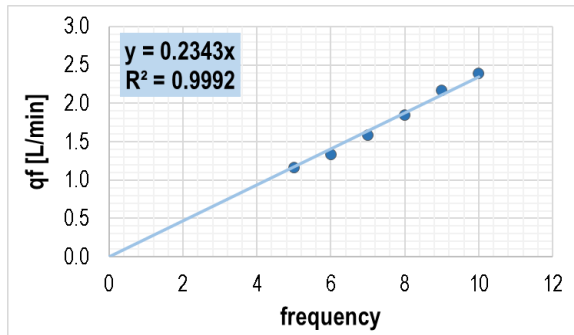


Figure 30. Pump calibration.

