

DEVELOPMENT OF ACID MODIFIED CELLULOSE ACETATE MEMBRANES FOR SALT WATER TREATMENT

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The main objective of this work has been to study the performance of membranes developed for water treatment. Polymeric membranes (CTP and CTP-Acid) were developed from solutions containing cellulose acetate (CA), cellulose triacetate (CTA) and polysulfone (PSF), using maleic acid (MA) and acetic acid (AA) as additives and chloroform/dioxane as solvent. The NIPS-type phase inversion method was chosen as the membrane film manufacturing technique. The incorporation of 2.5% and 5% by weight of acids in the membrane mixture allowed us to study the additive effect on the morphological structure, and to predict the performance of the membranes formed. The characterization of the membranes was performed by SEM and FTIR analyses. Examining the flux, permeability and selectivity of the membranes also permitted to study the efficiency and performance of each membrane. The addition of AA and MA additives within the mixture increased the hydrophilic character and improved the flux rate by increasing it from 75 Lm⁻²h⁻¹ to 142.74 Lm⁻²h⁻¹ for 5% maleic acid addition. The 5% CTP AA membrane gave very satisfactory results in terms of selectivity, with a maximum removal of 84% of NaCl salt. Therefore, this membrane has been considered to be the most efficient one, with a flux of 120 Lm⁻²h⁻¹ to 15 bar and a NaCl salt retention that meets the standards required by the World Health Organization (WHO).

Keywords: cellulose acetate (AC), acetic acid AA, maleic acid, additives, solvent treatment, brackish water

INTRODUCTION

Access to sufficient quantities of water for domestic consumption, as well as for business and industrial processes, is essential for human health and well-being. As the world population grows, the availability of fresh water is decreasing. Though around 71% of the Earth's surface is covered by water, 97.4% of it is seawater and only 2.6% is freshwater.¹ With the advancement of desalination technologies, seawater has become an attractive water source to cope with the scarcity of freshwater. This process can be applied anywhere a reliable water source is needed. Likewise, the elimination of brine must be studied and designed on a case-by-case basis, because it can be an environmental and economic problem in certain areas where flora and fauna are sensitive to the increase in the salinity of local seawater.²

The most widely applied and commercially available technologies for seawater desalination can be divided into two types: membrane processes and thermal processes. Reverse osmosis (RO) and nanofiltration (NF) are currently the main seawater desalination solutions. Scientific and technological advances relating to key membrane process equipment, namely: membranes, pumps, energy cost recovery device, have made the process energy efficient, which translates into low investment costs and low operating costs.³

The membrane constitutes the key element of the membrane process, its properties and performance depend closely on its morphology. For this reason, controlling the texturing processes to give it ultra-, micro-, or nanofiltration properties is the major goal of the manufacturer. The membrane must also have good mechanical, thermal and chemical resistance properties, or even have a surface layer with properties suitable for reverse osmosis, gas separation or pervaporation. Developing a transfer model is useful, as it makes it possible to formalize the phenomena involved

(thermodynamics, transfer, transport) and then to predict the paths of the compositions under development.²

Schützenberger was the first to synthesize cellulose acetate in 1865 by reacting acetic anhydride with cotton cellulose heated in a closed tube at 180 °C. Large-scale production has taken place from the early 1920s to the present day. In the most conventional acetylation process, native cellulose fibers are gradually converted into cellulose acetate under the action of a mixture of glacial acetic acid and acetic anhydride in the presence of a catalyst, such as sulfuric acid or perchloric acid.⁴

Asymmetric cellulose acetate membranes were widely used between the 1960s and 1980s, mainly for pure water for industrial processes and ultrapure water for semiconductor industries, and some of them are still in use today, with the advantage of a high resistance to chlorine.⁵

Although cellulose is hydrophilic, its derivatives are not necessarily hydrophilic. For instance, cellulose triacetate has a static contact angle with water of more than 60 degrees, making it essentially non-hydrophilic, with a good permeability to water. It is inexpensive and easy to manufacture.⁶⁻⁷ The physicochemical properties of this polymer depend on the degree of acetyl substitution (denoted DS), which also represents the mass content of acetyl groups. This is between 0 and 3.⁸⁻¹⁰ However, it is likely to be compressed under high operating pressures, more specifically at high temperatures, resulting in reduced output flux. Cellulose acetate has a lower hydrogen bonding tendency and therefore, lower crystallinity, which allows it to be soluble in common organic solvents, such as dioxane, acetone, chloroform, acetic acid.^{4,11}

The cellulose acetate membrane has experienced a great boom in the field of treatment of different types of water and several works have been carried out in this direction. For example, Fahhame Jazini and his team made membranes from a mixture between two copolymers of cellulose acetate and triacetate. The casting solution was prepared by dissolving CTA (3% by weight) and CA (12% by weight) in 1,4-dioxane (53.25% by weight) and acetone (17.75% by weight). Subsequently, methanol (10.3% by weight) and lactic acid (3.7% by weight) were incorporated as additives into the casting solution. The most efficient parameters, namely, post-casting solvent treatment, increased selectivity by 55% and increased water flux by 20%.⁸

In another study carried out with the addition of maleic acid and methanol, Thi Phuong Nga Nguyen and co-workers developed asymmetric flat membranes from cellulose acetate (CA) and cellulose triacetate (CTA). The casting solution comprised: 6.3 wt% CTA, 12.6 wt% CA, dissolved in 1,4-dioxane 49.9 wt% and 17.2 wt% acetone, with 3.7% by weight of maleic acid and 10.3% by weight of methanol as additives, at a thickness of 250 µm on a porous support; it was subsequently subjected to evaporation for 30 s at 25 °C and annealing at 85 °C. The optimized membrane showed a water flux of 10.39 L m⁻² h⁻¹, using a Milli-Q water filtration system and a 1 M NaCl feed solution. 9.270 L m⁻² h⁻¹ as the water stream, and a rejection of 99.533% NaCl was obtained, with a permeate of 0.1 M NaCl and a concentrate of 1 M KBr. They noted that the evaluation of the constituent polymers showed that higher CTA content led to greater salt resistance.¹²

In this context, the objective of this work consists in evaluating the efficiency of filtration membranes in order to treat brackish water. The first part is devoted to the synthesis of polymer membranes based on cellulose acetate (AC), polysulfone (PSF) and cellulose triacetate (TCA), using dioxane and chloroform as solvents; methanol and acids, such as acetic (AA) and maleic (MA) acids, as additives. The phase inversion method is chosen as the technique for producing membrane films. The membranes prepared were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), as well as by water absorption analysis. From the application point of view, several filtration tests were carried out with samples based on synthetic salt solutions to predict and study the performance of each membrane.

EXPERIMENTAL

Materials

The main materials used in our experiments and analysis were: cellulose acetate (AC) (Sigma Aldrich Chemistry USA, CAS No: 9004-35-7), with molecular weight ~50,000 g/mol (GPC); polysulfone (Psf) (Sigma-Aldrich, CAS No: 25135-51-7); cellulose triacetate (Sigma-Aldrich, CAS No: 9012-09-3). 1,4 Dioxane with a density of 1.03 g/cm³, CAS number: 123-91-1; chloroform or trichloromethane (CAS: 67-66-3); maleic acid (MA) (BIOCHEM Chemopharma France, CAS No: 110-16-7), acetic acid (AA) (VWR Chemicals, CAS No: 64-19-7).

Preparation of polymers (collodion)

The membranes were prepared by the NIPS phase inversion (solvent induced phase separation) method. The casting solution was prepared by dissolving CTA (5%), CA (6%) and Psf (4%) in 1,4-dioxane 54.25% and chloroform 15.75% in weight. Methanol (10% by weight) was added as an additive to the casting solution. The solution was stored in a BG vial. In the case of the modified membranes, acetic and maleic acids were added to the solution at two different concentrations (2.5 and 5% by weight), with stirring at 200 (rpm) for 4 h to homogenize the mixture. The viscous solution obtained was spread on a glass by adjusting the thickness of 150 μm using a molded knife (casting knife). Then followed the immersion of the membrane in a coagulation bath (ultrapure water was chosen as a non-solvent) and the treatment with alcohol diluted to 50% after drying the membrane for 6 hours. The percentage of polymers and chloroform remained constant for all the membranes synthesized *in situ*. The corresponding weight percentages obtained are presented in Table 1. The different stages of membrane development (passing from collodion to the formation of the membrane film) are illustrated in Figure 1.

Characterization of membranes

Different characterization methods were used to determine the characteristics of the membranes prepared and to study the physicochemical modifications induced by the post-treatment.

Fourier transform infrared spectroscopy (FTIR)

Infrared spectroscopy is a tool for analyzing the chemical structure of a polymer. The vibrational energies of the chemical bonds measured make it possible to identify the nature of the functional groups present in the sample. The device used was a Nicolet Nexus Fourier transform spectrometer (mirror speed: $0.6329 \text{ cm}\cdot\text{s}^{-1}$, iris aperture: 100, DTGS detector), equipped with an ATR Diamond Golden Gate accessory with a fixed resolution at 4 cm^{-1} . The swept frequency range covered the mid-infrared range $400\text{-}4000 \text{ cm}^{-1}$. The spectra were acquired in transmittance mode (64 scans). Before each analysis, the measuring cell was continuously scanned by an air current. Spectra were obtained for dry membranes.¹⁰

Table 1
Collodion composition for synthesized membranes

Membranes	Composition (weight %)						
	CA	CTA	Psf	1,4 dioxane, %	MA, %	AA, %	Methanol, %
CTP	6	5	4	59.25	--	--	10
CTP AA 5%	6	5	4	54.25	--	5	10
CTP AA 2.5%	6	5	4	56.25	--	2.5	10
CTP AM 5%	6	5	4	54.25	5	--	10
CTP AM 2.5%	6	5	4	56.25	2.5	--	10

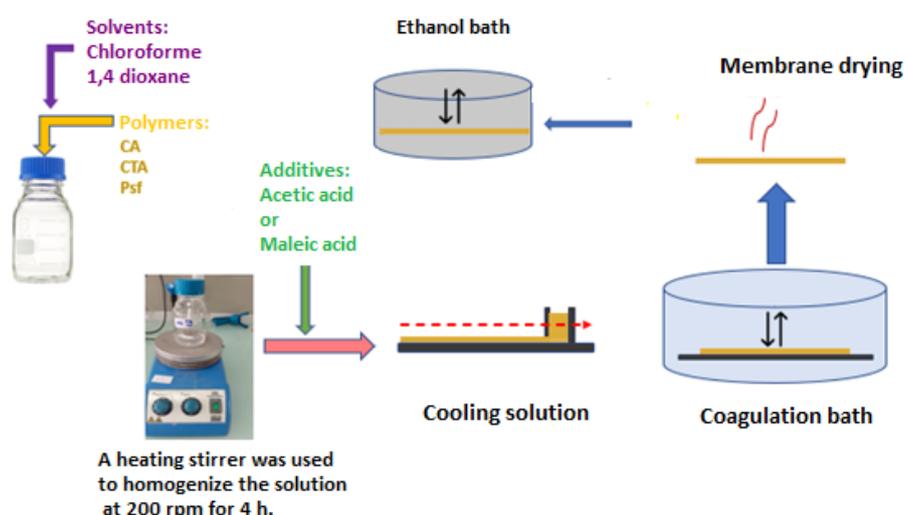


Figure 1: Polymeric membrane casting steps

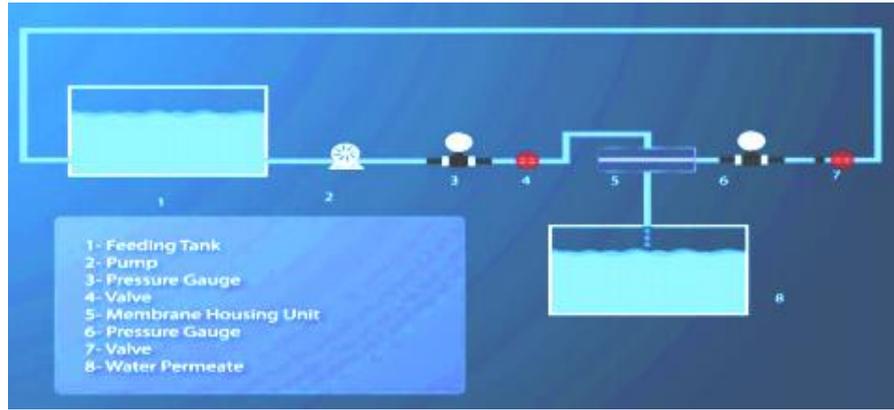


Figure 2: Diagram of the filtration test unit

Scanning electron microscopy (SEM)

It is a technique for observing the morphology of membranes, it consists of scanning the surface of the membrane with a beam of energetic electrons. The secondary electrons emitted by the irradiated sample are analyzed by a suitable detector, which makes it possible to reconstruct the image of the surface. The device used was a Zeiss-EVO Ma10 (Oberkochen, Germany), with a field effect of 1.5 nm resolution at 15 kV.

Water absorption (water uptake test)

To assess the hydrophilic/hydrophobic character of the membranes, it was considered useful to study the character of wettability by water absorption. To obtain the wetted membrane weight W_w , the membrane films were soaked in water for 24 h, dried with paper tissue and weighed. Then, they were dried in an oven at a temperature of 80 ° C for 24 hours and weighed again to obtain the weight of the dry membrane. From three values, the percentage increase in water consumption was calculated using the following Equation (1):⁸

$$\text{Water up take \%} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where W_w is the weight of the wet membrane, W_d is the weight of the dry membrane.

Physical characterization

Frontal filtration experimental device

The filtration system is shown in Figure 2. It is composed of a filtration cell called a test cell, accommodating flat membranes of 0.059 m in diameter, corresponding to a useful surface area of 0.0027 m². The cell is made up of three openings: feed, concentrate and permeate, connected to a high-pressure pump. All the measurements were carried out at transmembrane pressures of 25 bars. The permeate was collected in a beaker.

The concentrations of the permeate were determined either by the conductivity meter (in the case of a simple salt solution), or by the spectrometer-based method. Equation (2) was used to measure the flux of pure water, known as pure water permeability (PWF), and that of the solutions to be treated:

$$J_p = \frac{V}{\Delta t \cdot S} \quad (2)$$

where J_p is the pure water permeation flux (Lm⁻² h⁻¹), V is the volume of permeate in (L), S is the effective membrane surface area (m²) and Δt is the time (h).

The rejection rate of a species (noted TR) is defined as the percentage of species retained by the membrane. In the case of complex mixtures, an individual release rate is defined for each type of solute.⁵ The rejection rate was calculated using Equation (3) shown below:

$$T_R = 1 - \frac{C_p}{C_f} \cdot 100 \quad (3)$$

where C_p and C_f represent concentrations in the permeation and feed solution, respectively (wt%).

RESULTS AND DISCUSSION

FTIR analysis of membranes

Fourier transform infrared spectroscopy is one of the best suited techniques in the identification and analysis of membranes and mixtures, since it allows all the characteristic bands of the different functional groups of polymers to be demonstrated, as well as the specific interactions of the hydrogen bond type likely to develop between the various functional groups within the mixtures. This technique made it possible to confirm the presence of all the functional groups present in the CTP membranes

unmodified and modified by acetic acid AA (2.5 and 5% by weight of AA) and maleic acid (diacid type) MA (2.5 and 5% by weight of AM).

In the region of $4000\text{-}2000\text{ cm}^{-1}$ illustrated in Figure 3, the CTP membrane (without acid additive) exhibits a peak located around 3476 cm^{-1} , characterizing the overlap of two vibrations. The first attributed to the OH group linked with C=O groups by hydrogen bonding and the second corresponds to the free O-H group. The incorporation of acids into mixtures of modified CTP membranes shows a decrease in the wavenumber of the latter, as well as a very strong widening of the corresponding absorbance band, it characterizes the hydroxy-ester and carboxylic interactions. It has been found that, within the same membrane, by increasing the acid level from 2.5 to 5%, this band shifts towards the lowest wavenumbers at 3466 cm^{-1} , confirming that the acid-acid dimeric interactions are more important than hydroxy-ester interactions within modified CTP membranes. Also, the bands located between 2700 and 3100 cm^{-1} are attributed to the mode of vibration stretching of bonds, such as the OH of the associated carboxylic acid functions, as well as of the CH bonds of the hydroxyl groups of the phenol function of aromatic nature, which is due to intramolecular solvent-polymer interactions.⁹⁻¹²

In the area $1790\text{-}1650\text{ cm}^{-1}$, the characteristic bands of cellulose acetate and of cellulose triacetate are visible in the spectra of Figure 4 – a peak centered at 1741.16 cm^{-1} , which describes the grouping of the free ester C=O was observed in this region. The latter widens when introducing maleic acid and acetic acid in the mixtures. This is explained by the presence of a characteristic band of the vibration of monomeric carboxylics and the formation of an acid-acid (dimeric) interaction around 1703 cm^{-1} , which overlaps with that of the acid-ester interactions that does not appear because of the low level of acids in the mixture.¹³⁻¹⁶

Scanning electron microscopy (SEM) study

The morphology of the upper surfaces of the different membranes was analyzed by scanning electron microscopy (SEM) at a magnification of $10\text{ }\mu\text{m}$. The results are illustrated in Figure 5. The image of the CTP membrane in the absence of additive shows a compact film, with no pores, and not very smooth in appearance. Meanwhile, upon the incorporation of acids, the modified membranes have a fairly porous structure and surface swelling. It should be noted that when the acid level increases from 2.5 to 5% by weight, surface changes or pore size increases have been observed, including a higher number of pores on the surface.¹³

In summary, the incorporation of acids into the mixtures reduces the relatively compact appearance of the unmodified CTP membrane and provides a homogeneous, porous and symmetrical surface morphology for the modified CTP membranes.

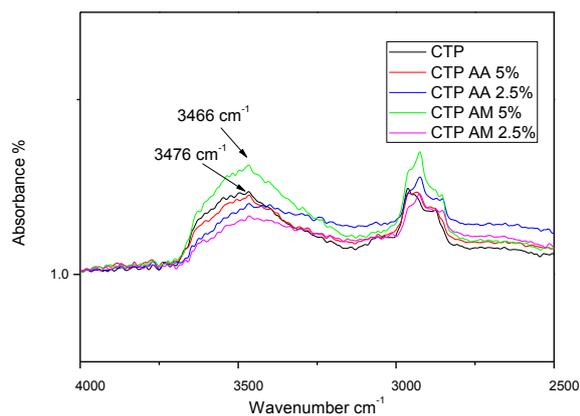


Figure 3: FTIR absorbance spectra of different membranes in the $4000\text{-}2000\text{ cm}^{-1}$ range

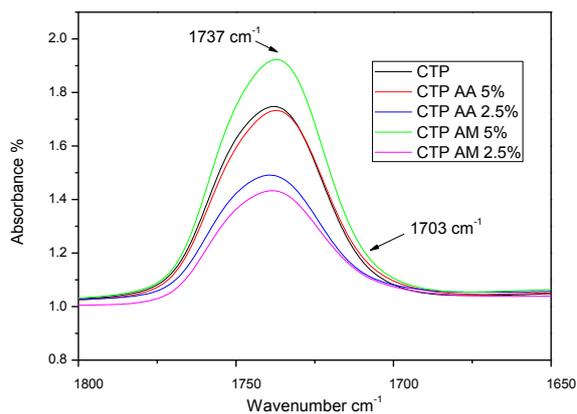


Figure 4: FTIR absorbance spectra of different membranes in the $1800\text{-}1650\text{ cm}^{-1}$ range

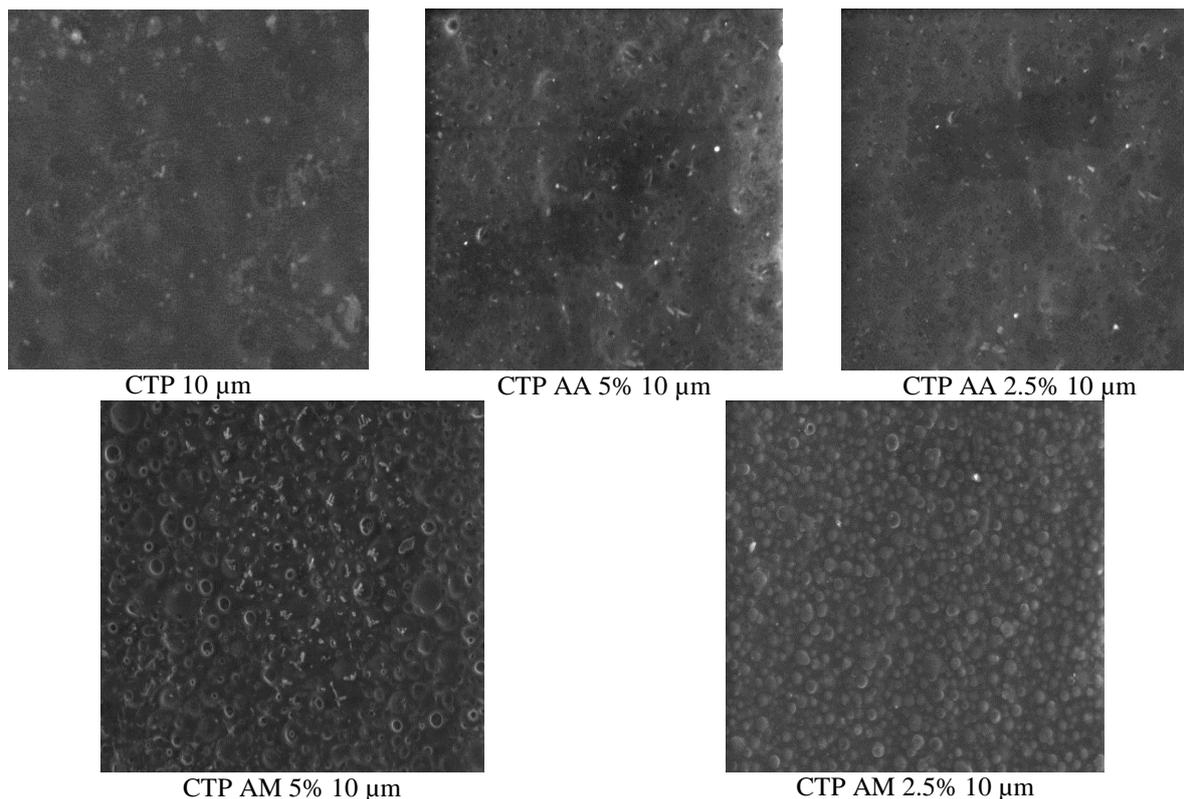


Figure 5: SEM images at 10 μm for membrane surfaces

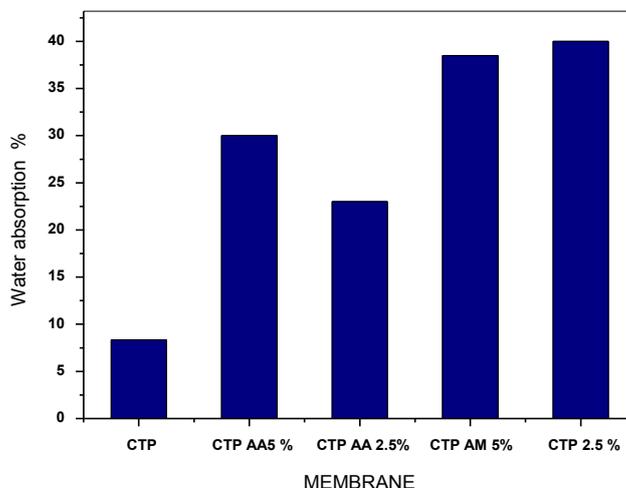


Figure 6: Water absorption of membranes CTP, CTP AA 5%, CTP AA 2.5%, CTP AM 5% and CTP AM 2.5%

Water absorption analysis

The wettability by water absorption was studied for the different membranes in order to determine their hydrophilic/hydrophobic nature. The wettability determines the ability of the membrane to absorb water at the membrane surface.^{17,12} The water absorption behavior of the membranes is presented in Figure 6. It is important to point out that this property is of the order of 8.33% for the unmodified CTP membrane, while it becomes more and more important for the modified membranes, and increases by increasing the level of acid in the mixture. The membrane having 5% by weight of maleic acid CTP MA 5% exhibits maximum water absorption. It is 5 times greater than that of the raw CTP membrane. In summary, the hydrophilic character is proportional to the water content. Its percentage increases by introducing the acid into the mixture, thus confirming that the latter acts as an additive and the membranes acquire a rather hydrophilic character. In fact, the -OH groups present in the structure, on

the surface of the modified membranes, interact with water via van der Waals forces and hydrogen bonding, so that the wettability increases.¹⁸⁻²¹ These results correlate with those obtained by SEM.

Membrane performance

Study of permeability to pure water

The plot of the permeation of pure water as a function of time illustrated in Figure 7 indicates that the flux of pure water (PWF) from the initial CTP membrane (without additives) is approximately $74.94 \text{ L m}^{-2} \text{ h}^{-1}$ at 15 bars. The influence of the AA acetic acid content in the synthesized polymer solution was studied on the water flux ($L_p \text{ m}^{-2} \text{ h}^{-1}$). The incorporation of 2.5% by weight of this acid improves the flux, it is around $118.61 \text{ L m}^{-2} \text{ h}^{-1}$ and reaches $133.74 \text{ L m}^{-2} \text{ h}^{-1}$ for a weight of 5% of the acid. In the same context, maleic acid (MA) improved the flux, which rose from 123.43 to $142.74 \text{ L m}^{-2} \text{ h}^{-1}$. It is twice higher than that of the initial CTP membrane, therefore demonstrating that the incorporation of the acids improved the hydrophilicity of the membrane, which also facilitated the diffusion of water through the membrane and thus improving the membrane flux. It was also found that the membrane having 5% AA exhibits a better flux than the membrane composed of 2.5% by weight of MA. This phenomenon can be explained by the inaccessibility of certain OH groups, which promote dimeric interactions to the detriment of the interactions with the water molecule. These results are in good agreement with those obtained by FTIR. In summary, the performance of the membrane from the point of view of the flux has been improved by incorporating the acids into the solutions and the efficiency of the membranes based on maleic acid is better than that of the acetic acid based ones for the same concentration at the same pressure.

It was noted that the hydraulic permeability of the membranes prepared from 2.5% and 5% by weight of acetic acid slightly increases, respectively from 6.25 to $6.51 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. It is estimated between 6.65 to $7.12 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for a percentage of maleic acid ranging from 2.5 to 5%. For this reason, it can be deduced that the permeability L_p increases with the increase in the additive concentration, and the best hydraulic permeability was obtained for the membrane composed of 5% maleic acid. It is important to note that the values obtained for the permeability are adequate NF membranes, considering the values reported in the literature between 5 - $100 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$.

In conclusion, the incorporation of acid additives, regardless of their concentration in the molding solution, increases the rate of water penetration into the membrane. The water flux of the modified membranes is higher than that of the unmodified membrane, due to the improved hydrophilicity of the membranes.¹⁸ These results are in agreement with the SEM images and correlate with the study of water absorption.

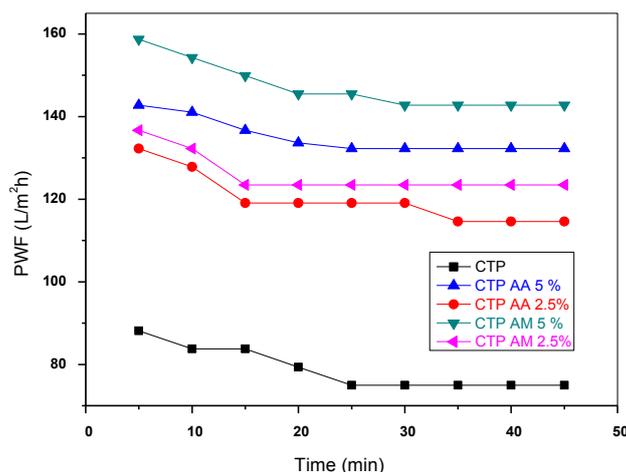


Figure 7: Evolution of pure water flux (PWF) as a function of time (min) at 15 bars

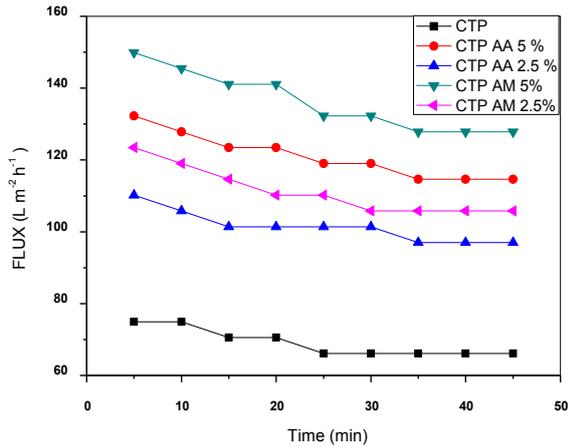


Figure 8: Variation of flux as a function of time for 5 g/L of NaCl

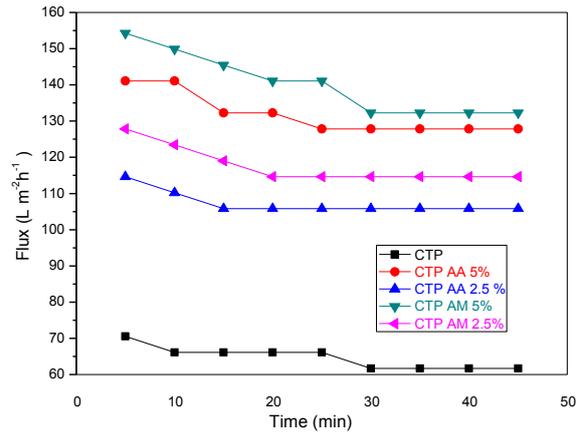


Figure 9: Variation of flux as a function of time for 10 g/L of NaCl

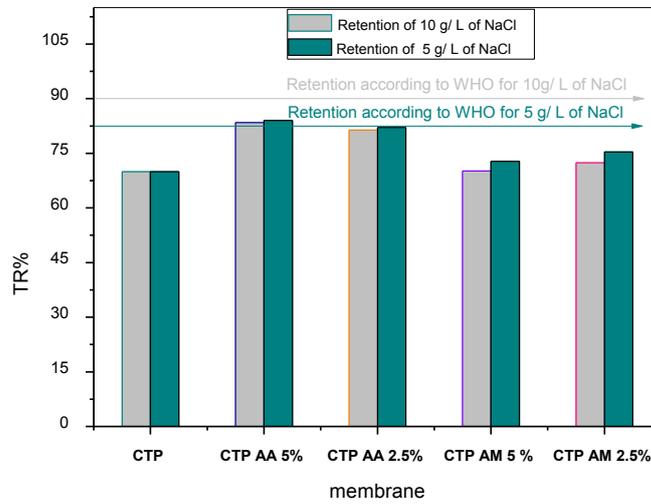


Figure 10: Retention rate of NaCl salt by the membranes

Salt retention studies

The study of the selectivity mechanism of the membranes prepared was carried out for synthetic solutes containing monovalent NaCl ions. The influence of the filtration operating conditions was studied by determining the retention rate of the various ions present in the solution, as a function of the pressure applied and of the concentration of the feed solution.

Membrane permeability to saline solutions

Figures 8-9 present the change in the flux of treated brackish water as a function of time for NaCl salt concentrations of 5 g/L and 10 g/L at a pressure of 15 bar. The results show that the permeate fluxes remain almost constant after 30 min for all the membranes. The variation in flux did not change, compared to PWF, for the different membranes, while the membrane with the maximum maleic acid showed the best flux. However, a loss of flux was observed for all the membranes in the two solutions. It has been found that this loss is greater for the more concentrated saline solution and for the modified membranes. The loss of flux density represents a decrease in flux values relative to the flux of pure water permeate (PWF). The biggest loss was estimated at 18.21%. It corresponds to the CTP AA membrane composed of 2.5% acetic acid, followed by the unmodified membrane with values of 16% and 13.33% for salt concentrations of 5 g/L and 10 g/L, respectively.

Selective separation of ions

The retention of the monovalent NaCl salt exhibited in Figure 10 reveals a retention of 69.97% for the unmodified CTP membrane at initial salt concentrations of 5 g/L and 10 g/L. This value increases, regardless of the nature of the acid added to the mixture and regardless of its concentration. It was also

found that the membrane of CTP MA 2.5% recorded a retention value of 72.4%, which is greater than that of the membrane containing 5% of MA – of 70.12%. This confirms the SEM results, which showed a higher surface porosity for the 5% MA CTP membrane, indicating better flux and lower retention. It was found that the removal of salt is more significant in the case of the membranes modified with acetic acid. The incorporation of 2.5 and 5% by weight of this acid gave a retention of 81.36% to 83.42% for NaCl concentration of 10 g/L, and of 82.26% and 84% for a concentration of 5 g/L. It is noted that the flux observed for the CTP AA 5% membrane, characterized by the best rate of elimination, is very satisfactory, being of $120 \text{ Lm}^{-2}\text{h}^{-1}$.

In summary, the salt elimination study for the different membranes allowed concluding that, in terms of selectivity, the AA2.5% CTP and AA5% CTP membranes showed more or less similar results, with maximum retention efficiency of NaCl salts for the 5% CTP AA membrane. This retention rate obtained remains insufficient to meet the required salinity standards of the WHO for a concentration of 10 g in NaCl. On the other hand, for a concentration of 5 g of NaCl, the obtained rates for the membranes based on acetic acid CTP AA meet the WHO standards for providing water of good quality.

In conclusion, in terms of their salts rejection rate, the membranes studied can be arranged in the following sequence: CTP AA 5% > CTP AA2.5% > CTP MA 5% > CTP MA 2.5% > CTP, regardless of the brackish solution. The 5% AA CTP membranes are considered to be the most reliable and efficient for the removal of monovalent salts from the point of view of flux. It presents the optimal parameters, for a flux of $120 \text{ Lm}^{-2}\text{h}^{-1}$ at 15 bars and a NaCl salt retention of around 83.42%.

CONCLUSION

AC/TAC/PSf/Acid organic polymer membranes were prepared by using the phase inversion technique induced by coagulation in a water bath (NIPS), followed by drying with ethanol. Acetic acid and maleic acid, as well as methanol, were used as additives, while chloroform and dioxane as solvents. The essential results of the study are summarized below.

The FTIR analyses confirmed the presence of the characteristic bands assigned to the functional groups of the various components of the mixture in all the membranes produced. The SEM results suggested that the incorporation of additive acids, such as acetic acid and maleic acid, improved the membrane surface. On the other hand, the drying by solvent exchange, as well as the increase of acid contents in the mixture, led to the formation of pores and, therefore, the membranes exhibited higher and satisfactory flux permeation. In terms of flux and selectivity, satisfactory results have been obtained: the incorporation of acetic acid and maleic acid into the initial CTP membrane improved the permeability flux. The 5% AA CTP membrane has been considered to be the most reliable and efficient formulation for the selective removal of monovalent salts. It has the optimal parameters, for a flux of $120 \text{ L m}^{-2}\text{h}^{-1}$ at 15 bars, and a NaCl salt retention of around 84% for a salt content of 5 g/L, which meets WHO standards.

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