CELLULOSE CHEMISTRY AND TECHNOLOGY

PERFORMANCE OF CARBOXYMETHYL CELLULOSE/POLYSULPHONE MEMBRANES PREPARED VIA DIFFERENT IMMERSION METHODS FOR SALT RICH WATERS

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The main objective of this work has been to carry out the synthesis of composite membranes from carboxymethyl cellulose (CMC)/polysulfone (PSf) by the crosslinking of glutaraldehyde (GA) or lactic acid (LA), using the non-solvent induced phase separation (NIPS) method. The effects of different parameters, such as the type and degree of crosslinking, the immersion method, and the coating procedure, including the thermal treatment have been studied. The prepared membranes were analyzed in terms of water absorption and flux, as well as their efficiency in retaining salt ions from synthetic waters rich in mono/divalent salts and real seawater samples. The optimized membrane containing 2% by weight of CMC and 2% of lactic acid as crosslinking agent, coagulated by immersion for 10 min, represented a rejection efficiency of 97.3%, 88.3% and 34% for the solutions of $MgSO_4$, $CaCO_3$ and NaCl, respectively. The optimal membrane recorded a pure water flux of 127.37 L/m^2h, under a low transmembrane pressure of 10 bars, and permeability of 26 L/m^2 h bars. The membrane flux recovery rate was greater than 94%, indicating satisfactory resistance to fouling.

Keywords: carboxymethylcellulose (CMC), coating, crosslinking, composite membrane, lactic acid, glutaraldehyde

INTRODUCTION

Although the total mass of water on our planet represents 1380 million km^3, it is made up of 97.2% sea water and 2.15% ice, which cannot be used directly, and only 0.07% fresh water is easily available from lakes, rivers and certain underground waters, *i.e.* about one million km^3. However, the distribution of this water is very uneven. In fact, ten countries share 60% of the freshwater reserve and twenty-nine others, mainly in Africa and the Middle East, are on the contrary, facing a chronic shortage of fresh water. In these countries, according to the Water Resources Institute, 250 million people do not currently have the minimum vital water defined as 1000 m^3 per capita per year. 400 million people live in a situation of water stress, estimated at between 1000 and 2000 m^3 per capita per year. It is estimated that 2.5 billion people could suffer from water shortage in the year 2050 given population growth, climatic hazards and high consumption of water by the different socio-economic sectors.[1] To cope with this problem, new techniques for producing drinking water will have to be applied to meet the needs of the growing population.

One of the promising techniques in the field of water treatment, which has experienced great development throughout the world, is seawater or brackish water desalination. Seawater desalination techniques have been operational for many years. However, in recent years, the capacity of desalination plants has increased sharply, while operation costs have decreased significantly.[2-3]

The techniques generally used to desalinate sea and brackish water are thermal and membrane processes.[4] Membrane technology is emerging as a viable method for molecular separation offering many advantages over conventional methods.[5] It consumes less energy, requires less space and can be used in a much simpler way. It consumes up to a tenth of the energy currently used for conventional distillation.[6-8] Its application has been extended to a wide range of fields, including medicine, chemistry, chemical technology and chemical engineering. Membrane technology has received particular attention for wastewater treatment, as micro/ultra/filtration can reject particles, colloids and macromolecules and aid in disinfection.

After the significant commercial success of reverse osmosis (RO) and ultrafiltration (UF), membranes with separation characteristics between these two technologies are expected to be promising financially. Such membranes are called nanofiltration (NF) membranes. It is an essential technique in the food, chemical and pharmaceutical industries.[3,7] Typically, NF membranes involve the separation of salts (monovalent and divalent) and/or organic solutes. It is becoming a viable alternative to conventional water treatment technologies, because it can operate at lower pressures, provide high flux, and be more energy efficient than RO systems. It has been shown that twice the permeate throughput can be obtained with NF compared to RO. Besides, by replacing RO with NF membranes, about 20% electrical energy can be saved.[9-10]

Sodium carboxymethylcellulose (CMC-Na) is a negatively charged semi-flexible linear polyelectrolyte. It is a derivative of the most abundant biopolymer on Earth – cellulose, formed by replacing some of the hydroxyl groups in cellulose with carboxymethyl groups.[11] Due to its wide availability, as well as its thickening and swelling properties, it is widely used in many industries, such as food, pharmaceutical, household and personal care products, as well as the paper industry, paints, water treatment and mineral processing. The diversity of chemical structures allows the development of advanced functionalized materials that can meet various expectations. It was among the first used to make biocompatible hydrogels for biomedical applications.[12]

Behrouz *et al.*[13] studied the application of carboxymethylcellulose in the desalination of sea water. Composite nanofiltration membranes were prepared as CMC/PES thin layers, using glutaraldehyde for *in situ* crosslinking. Thin-film composite nanofiltration (TFC-NF) membranes, containing 0.2 wt% CMC, with 20% crosslinking degree and 10 min soaking time, showed the optimal performance with a pure water flux of 47.90 ± 1.77 L/m^{2}h. The optimal membrane rejected 91.90%, 68.63% and 45.90% of Na_2SO_4, $MgSO_4$ and NaCl solutions (100 mg/L), respectively, indicating its good desalting performance under low pressure. Moreover, the flux recovery ratios (FRR, %) increased from 46.83% for the PES support to 76.48% for the optimal TFC-NF membrane, indicating a significant improvement in antifouling performance due to the crosslinking of the CMC on the support membrane.

V. Hoseinpour *et al.*[14] synthesized PES membranes modified with carboxymethylcellulose derivatives. Carboxymethylcellulose (CMC) and sulphated carboxymethylcellulose (SCMC) were immobilized on the surface of amino PES membranes (PES-NH_2) via amide bonds to synthesize PES-CMC and PES-SCMC membranes, respectively, and the concentration of immobilized CMC and SCMC was determined. The results showed a decrease in contact angle, protein adsorption and platelet adhesion in the case of PES-CMC and PES-SCMC, compared to unmodified PES membranes, which supported the increased hemocompatibility of modified membranes, in particular for the PES-SCMC membrane. In addition, PES-CMC and PES-SCMC membranes showed good antifouling properties, especially for PES-SCMC.

The present work aims at improving the performance of a UF membrane based on polysulfone (PSf) by introducing molecules with different properties, such as CMC-Na, in order to obtain a more efficient nanofiltration membrane. The efficiency of the prepared membranes was investigated by studying the effects of different parameters, such as the type of coagulant, crosslinking agent, coating and thermal treatment. Membranes were prepared using the NIPS phase inversion procedure. Glutaraldehyde (GA) and lactic acid (Al) were used as crosslinking agents in a solution containing sodium carboxymethylcellulose (Na-CMC), producing a crosslinked network and forming insoluble membranes based on polysulfone. The obtained membranes were then tested in a laboratory filtration system in order to carry out a quantitative study on the transfer of matter in terms of flux and selectivity for samples of synthetic waters rich in mono/divalent salts and real seawater samples. Other parameters were also examined, such as water absorption and clogging, which have an impact on the life of the membrane and its performance.

EXPERIMENTAL

Materials

Sodium carboxymethylcellulose (CMC-Na) (CAS No: 9000-11-7), and polysulfone (Psf) (CAS No: 25135-51-7) were purchased from Sigma Aldrich (Germany), and used as polymers in the casting solution. Polyvinylpyrrolidone (PVP), N,N-dimethylacetamide (DMAc) were purchased from Fluka and Biochem, respectively, and used as solvents for the polymers mentioned above. Lactic acid (LA) and glutaraldehyde (GA) were purchased from Sigma Aldrich, and used for agent reticulation. Salts such as NaCl (sodium chloride), $CaCO_3$ (calcium carbonate) obtained from Biochem Lab and $MgSO_4$ (magnesium sulfate) purchased by Sigma Aldrich, were used to prepare saline solutions in order to study membranes' selectivity and evaluate their performance.

Membrane manufacturing

Membranes were prepared by the phase inversion method NIPS (solvent-induced phase separation).[11] Polymer blend solutions were prepared from 18 wt% polysulfone (PSf) and 1 wt% polyvinylpyrrolidone (PVP) in 81 wt% N,N-dimethylacetamide (DMAc) solvent, under constant stirring, at 300 rpm for 24 hours, at a temperature of 50 °C. A homogeneous solution was obtained and then left without stirring for 30 minutes to eliminate air bubbles. The formulation was spread on a glass plate using a casting knife with a thickness of 150 µm. Finally, the glass plate with the membrane solution was immersed into different coagulants at different concentrations.

The coagulation step is the most important in the manufacture of membranes. It is done either directly in water or in a solution of CMC-Na-X, where X stands for lactic acid or glutaraldehyde (Table 1). The polymer film is transformed by progressive coagulation, from a liquid phase (transparent color) to a solid phase (whitish color), detaching from the glass plate. After 17 min, the membrane film was placed in a bath of demineralised water for 24 h to accelerate the exchange between solvent and non-solvent. Some films underwent thermal annealing at 80 °C in an oven for 10 min. Only the PCAR membrane was prepared by spreading a CMC-LA solution on a PSf film for coating it. After the excess of this solution was removed, the membrane was treated in the oven in the same way as the other membranes. All the membranes were stored in distilled water. The compositions of the membranes are shown in Table 1, and the structures of their components – in Figure 1.

Characterization of filtration membranes

Volume flux

The permeation flux (also called permeation velocity) is a unit permeation rate, *i.e.* the ratio between the volumetric permeation rate (V) and the effective surface of the membrane:[15]

$$Jp = \frac{V}{\Delta t.S} \tag{1}$$

where Jp is the pure water permeation flux (L/m^2h),V is the volume of permeate in (L), S is the effective membrane surface area (m^2) and t is the time.

Table 1

Blend composition (% weight) and treatments applied in the fabrication of the membranes

Membrane symbol	PSf	PVP	DMAc	CMC-Na	X=GA	X=LA	Observation
PCAR 2-2%	9	0.5	40	2%	/	2%	R: coating by CMC-X
PCAE 2-2%	9	0.5	40	2%	/	2%	E: immersed in water for coagulation
PCAS 2-2%	9	0.5	40	2%	/	2%	S: immersed in CMC-X solution
PCAS 2-4%	9	0.5	40	2%	/	4%	S: immersed in CMC-X solution
PCAF 2-4%	9	0.5	40	2%	/	4%	F: oven dried for 10 min
PCGS 2-2%	9	0.5	40	2%	2%	/	S: immersed in CMC-X solution
PCGE 2-2%	9	0.5	40	2%	2%	/	E : immersed in water for coagulation
PCGS 2-3%	9	0.5	40	2%	3%	/	S: immersed in CMC-X solution

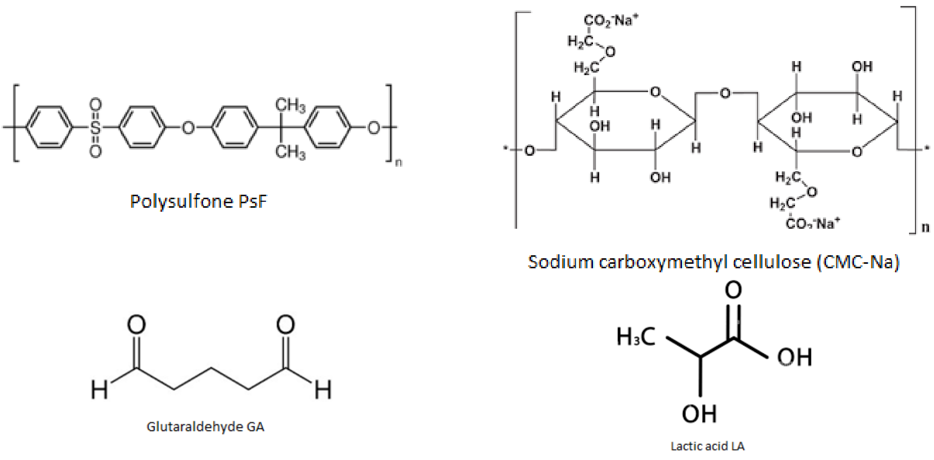


Figure 1: Chemical formula of compounds used for membrane preparation

Hydraulic permeability of membranes

Permeability (Lp) is an important criterion that influences the membrane performance as it indicates its productivity. It is defined as the volume flux rate of liquid passing through a unit area of membrane for a unit transmembrane pressure. The slope of the line Jp = f (ΔP) corresponds to the permeability of the membrane to distilled water. The relation between the permeate flux Jp and the transmembrane pressure ΔP is given by Darcy's law:[16-17]

$$\mathrm{Lp} = \frac{Jp}{\Delta \mathrm{P}} \tag{2}$$

Salt rejection

The salt rejection of a species (denoted T_R) is a dimensionless quantity defined as the percentage of species retained by the membrane. Two saline solutions were studied: the first was a synthetic solution and the other – a saline solution obtained from a real seawater source from Fouka – Tipaza. In the case of complex mixtures, an individual rejection rate is defined for each type of solute.[18-19] The salt rejection was calculated using Equation (3) shown below:

$$\mathrm{T_R} = 1 - \frac{C_P}{C_f} \times 100 \tag{3}$$

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

Water absorption

To evaluate the hydrophilic or hydrophobic character of the membranes, it is essential to study their wettability. Thus, the membrane films were soaked in water for 24 h, then dried with paper and weighed. After this, the membranes were dried in an oven at a temperature of 80 °C for 24 hours and then weighed again to obtain the dry membrane weight. From three values, water absorption percentage increase was calculated using the following equation:[19]

$$\text{Water absorption\%} = \left(\frac{W_w}{W_d} - 1\right) \times 100 \tag{4}$$

where W_w is the wet membrane's weight, W_d is the dry membrane's weight.

RESULTS AND DISCUSSION

Membrane performance study

It is essential to study the membranes' performance to determine their effectiveness. Therefore, several parameters were evaluated, namely, permeability to pure water, flux and selectivity. The determination of the permeability to pure water (PEP) is the simplest analysis that provides a general idea of the usage properties of the membranes studied. In addition, it constitutes the reference state of the membrane. Its periodic measurement (before, after use and cleaning of the membrane) makes it possible to assess the importance of clogging and the effectiveness of the unclogging agent.[20-21]

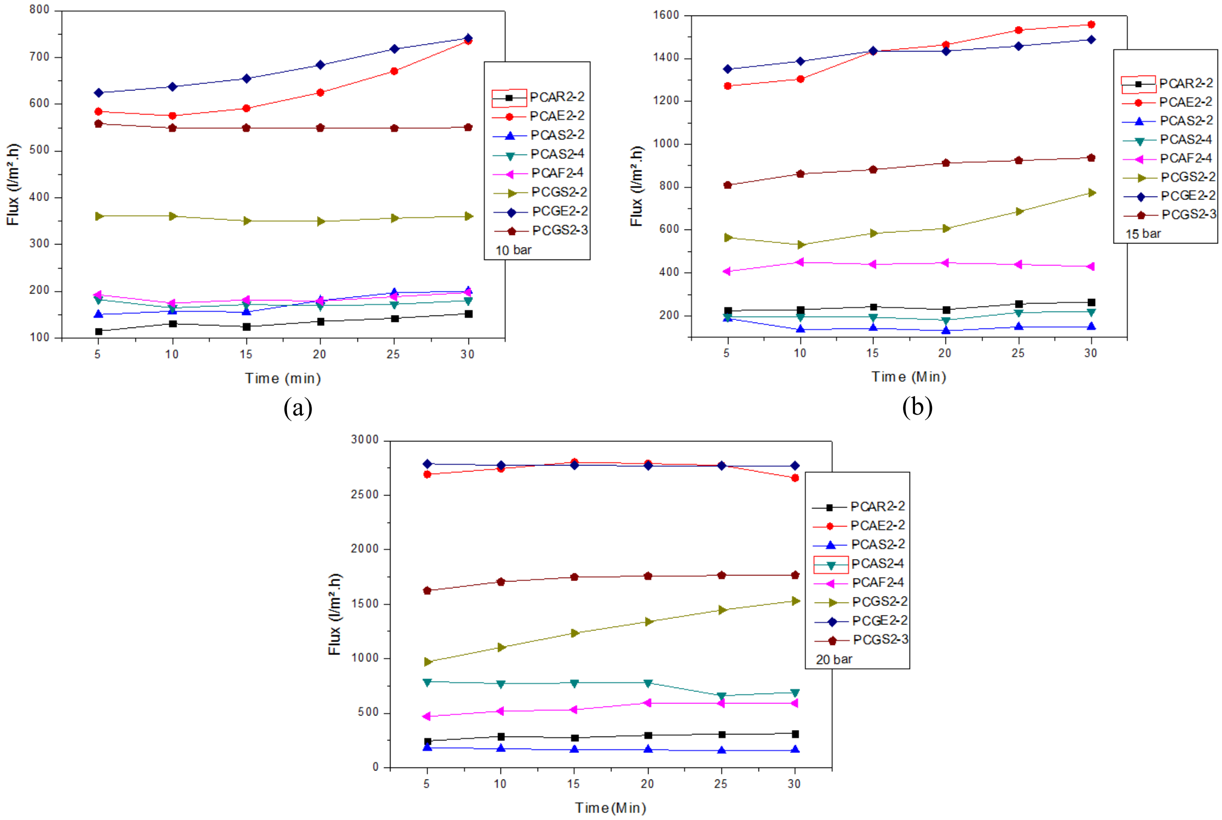
Study of pure water permeability

The plots of pure water permeability versus time are shown in Figure 2, revealing that the pure water flux from the PCA and PCG membranes, formed by immersion in water as the first coagulant, gave the best flux for the different pressures used. It is around 744.37 L/m² h at 10 bars for a time of 30 min.

The PCAR 2-2% membrane has the lowest flux, with a value of 127.37 L/m² h at 10 bars, with similarly low values at higher pressures, namely at 15 and 20 bars, of 231.42 and 267 L/m² h, respectively. It has also been observed that the increase in the concentration of lactic acid in the solution, regardless of the preparation procedure of the membranes, leads to similar flux values for the pressures of 10 and 15 bars; the difference is greater for pressures of 20 bars. On the other hand, the PCA membranes first immersed in water as a coagulant recorded pure water permeability flux values which are threefold (3.35) those of membranes with an identical acid concentration.

Regarding the membranes based on 4% lactic acid (PCA 2-4%), the influence of thermal treatment on the permeability of the membranes to pure water was examined. It was found that the latter is lower for the membrane that had been dried for 10 minutes in the oven. This difference is clearly seen itself at pressures of 15 and 20 bars, where the PCAF membrane recorded values of 428.56 and 605.9 L/m² h, respectively, against values of 601.68 and 787.86 L/m² h at pressures of 15 and 20 bars, respectively, for the same membrane formulations, but which had not undergone heat treatment. This confirms previous findings according to which membrane pores shrink after heat treatment.[14]

Meanwhile, the PCGS membranes in direct contact with the solution gave higher pure water permeability values for higher contents of glutaraldehyde, whatever the pressure exerted. For example, the flux of the PCGS 2-2% membrane is equal to 348 L/m² h at 10 bars, whereas it is 670 L/m² h for the PCGS 2-3% membrane. Moreover, the PCG membrane immersed first in water as coagulant recorded the best flux values, whatever the concentration of glutaraldehyde or the pressure exerted.[22-23]



(a)

(b)

(c)

Figure 2: Variation of pure water flux as a function of time for all membranes at different pressure (a) 10 bars, (b) 15 bars and (c) 20 bars

Thus, the initial immersion of the membranes in distilled water for coagulation gives the best flux regardless of the crosslinking agent used or its amount. Also, it has been noted that the heat treatment of the membranes affects the permeation values. Similarly, the coating of the PSf-PVP membrane with CMC-LA solutions is not favorable to membrane permeation. Thus, membranes immersed in distilled water are the most efficient in terms of pure water flux, whatever the pressure applied.

Study of flux as a function of transmembrane pressure

The effects of pressure were studied for the differently synthesized membranes using ultrapure water. It is evident that, as the transmembrane pressure increases, the driving force of pure water penetration through the membrane is enhanced, hence the flux of each membrane grows linearly as a function of pressure, reflected by straight lines, obeying Darcy's law.[14]

Figure 3 illustrates the pure water flux of PCA and PCG membranes as a function of pressure. It may be noted that the flux of PCAS 2-2% and PCAR 2-2% membranes varies a little, recording values from 173.61 L/m².h and 133.379 L/m².h, for a pressure of 10 bars, to 203.54 L /m².h and 287.33 L/m².h at 20 bars, respectively. These results confirm that the coating tends to reduce flux. Indeed, a thin layer of CMC-LA on the PSf support decreases the pore size of the PSf membrane, leading to a decrease in permeate flux. A maximum flux equal to 2813 L/m².h at 20 bars was obtained for the membrane based on PCAE lactic acid. As for glutaraldehyde-based membranes, it has also been demonstrated that the flux in the PCAS (2-2%) membrane varies, it is 356.34 L/m².h for a pressure of 10 bars and 744.84 L/m².h at 20 bars. The best flux was obtained for the membrane PCGE2-2%, with values from 676.61 L/m².h, for a pressure of 10 bars, to 1640.57 L/m².h for a pressure of 20 bars.

Hydraulic permeability

Permeability is a key factor influencing membrane performance, as it defines its productivity. The volume flux rate of fluid flowing through a unit area of membrane is determined for a single transmembrane pressure.[24-25] The water permeability was established as a function of the transmembrane pressure,[26] following the evolution of the filtration rate. It was calculated from the slope of the line Jv = f (ΔP).

From Figure 4, it has been noticed that the membranes permeability is proportional to the flux. It represents the inverse of the hydraulic resistance of the membrane; the lowest permeability is Lp = 1.85 L/m²h bar obtained for the PCAS 2-2% membrane coagulated in the solution containing 2% CMC and 2% lactic acid, the coating leads to a low permeability value, of around 26.5 L/m².h bar. The best membranes in terms of hydraulic permeability were found to be PCXE membranes, thus confirming that water is the best coagulant. So, improving the hydrophobic character of the membrane will also facilitate the water diffusion through the membrane. In addition, the membrane having lactic acid as a crosslinking agent immersed in water has the highest permeability, of 146.58 L/m².h bar, whatever the percentage of crosslinking.

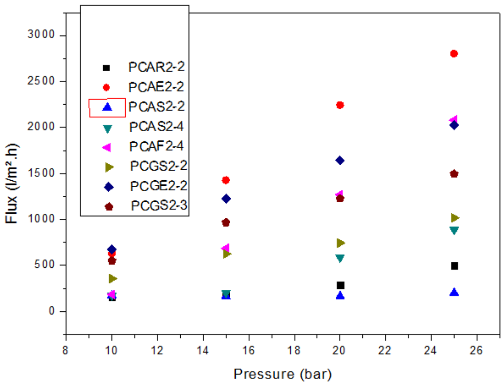


Figure 3: Flux variation as a function of PCA and PCG transmembrane pressure

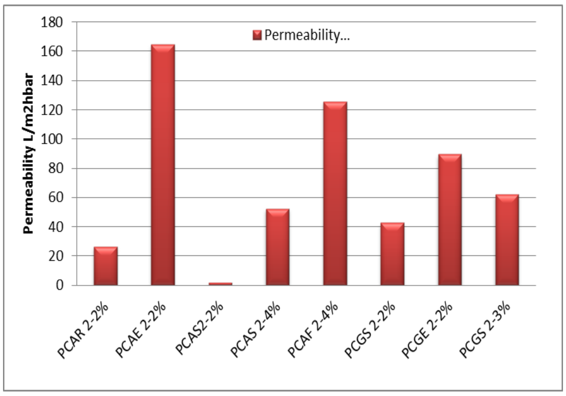


Figure 4: Permeability of PCA and PCG membranes

In conclusion, the incorporation of aldehyde and lactic acid type crosslinking agents into the formulation increases the rate of water penetration through the membrane. The water flux of the synthesized membranes is higher than that of pure PSf membranes, which are hydrophobic, regardless of the amounts of the compounds introduced into the formulation. This confirms previous research findings, according to which crosslinking agents play the role of pore formation agents in the solution, thus implying a low hydraulic resistance of the membrane.[27]

Water absorption

The water absorption behavior of membranes is illustrated in Figure 5, indicating that the highest water content was observed for the membranes with the lowest flux. The best absorption value, of 50%, was obtained for the PCAR 2-2% and PCGS 2-2% membranes, followed by the PCAF 2-4% membrane with a percentage of 42%. This can be explained by the phenomenon of swelling, which can occur at the surface of the membranes, and consequently affects both the permeation and the permeability to pure water.[13-28]

Permeation flux study of di-/monovalent salts

The study of di-/monovalent salt rich water flux illustrated in Figure 6 shows the evolution of the flux of synthetic water as a function of time at a pressure of 10 bars. The results reveal that the flux values of the synthetic solution remain constant for all the membranes, which exhibit the same behavior as in the case of the pure water flux. Also, the best flux of water rich in mono-/divalent ions was obtained for PCA and PCG membranes immersed in water as coagulant, reaching around 735.37 L/m² h for PCGE, while its flux for pure water was 744.37 L/m² h. On the other hand, the PCAR2-2% membrane recorded a flux value for pure water of 127.37 L/m² h, and for the salt-rich solution of 120.37 L/m² h at 10 bars. It is considered as the weakest flux, however, it presented an equal flux recovery of 94.5%.

Thus, all the membranes recorded lower flux values for the salt solution, compared to those for pure water. This can probably be due either to the concentration polarization, which leads to the accumulation of salt ions at the membrane surface, limiting the filtration flux, or it can be caused by membrane clogging.

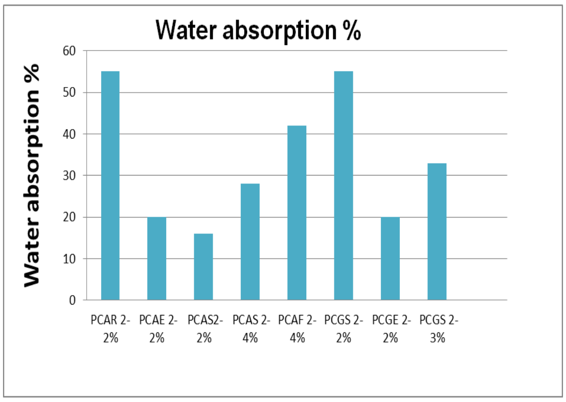


Figure 5:Water absorption of the membranes

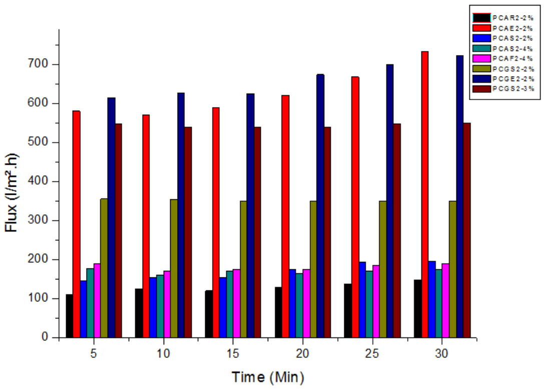


Figure 6:Variation of saline water flux as a function of time for all membranes

Study of the retention of $MgSO_4$, $CaCO_3$ and NaCl salts

The hardness of water indicates its concentration of dissolved minerals, particularly, of Ca^{2+} and Mg^{2+} ions, which are the major minerals present in most types of water.[17-18,29] The higher the concentration of these minerals, the harder the water is. However, hard water consumption has consequences for human health, as its high quantity of mineral salts can cause certain diseases, including cardiovascular ones. The presence of limestone is also responsible for the deterioration of certain household appliances (piping, water heaters, *etc*.).

Table 2 shows the initial salt concentrations and their retention rates corresponding to the each of the membranes tested. A high elimination rate of magnesium Mg^{2+} was observed for all the membranes, varying from 87% to 97.3%. For calcium, the rejection rate is lower, but still very satisfactory, being estimated between 70% and 88.3%, and thus, quite close to that of magnesium. The difference in the rejection rate between the two ions may be due to the hydrated radius of Mg^{2+}, which is larger than that of Ca^{2+}, which makes the retention of Mg^{2+} easier.

The data regarding the rejection of divalent ions by the prepared membranes shown in Figure 7 indicate that the membranes correspond to the requirements established by WHO freshwater standards (Table 3). The best divalent salt retention rate was obtained for the PCAR2-2% membrane, while the maximum elimination of Mg^{2+} is noted for the PCGS2-2% membrane.

On the other hand, the lowest calcium retention rate is obtained for the PCAF 2-4%

membrane, while the lowest rate of Mg^{2+} was obtained for PCAE2-2%, estimated at 86.6%. It is important to note that the performance of membranes treated by immersion into a 2% glutaraldehyde solution by weight is the most satisfactory. Also, it was found that the percentage increase in glutaraldehyde or lactic acid decreases the rejection rate. Thus, the salt rejection by the membranes was observed to decrease in the following order: $MgSO_4$>$CaCO_3$>NaCl.

The retention of the NaCl salt reaches the maximum peak of 34.8% for the membrane coated with the 2% lactic acid solution, and the minimum – for the membrane immersed into a solution containing the same quantity of this acid. It is the lowest level of retention, if all the salts used in the study are considered. The results obtained for the salt rejection cannot be explained only by a size exclusion mechanism, based on the idea that the size of hydrated ions is smaller than that of the pores of the membranes. According to Donnan's exclusion theory, the retention is also a consequence of electrostatic interactions between surface charges of the active layer of the membrane and ions in the solution. Thus, negatively charged membranes tend to repel multivalent anions (such as SO_4^{-2}) more than monovalent anions (such as Cl^-), while attracting multivalent cations (such as Mg^{2+}) more than monovalent cations (such as Na^+). It is noted that a negative charge can be induced in the selective layer by coating CMC molecules on the PS support. This charge can be attributed to the carboxyl groups of the CMC molecules, and therefore the salt rejection observed in this study can be explained by Donnan's exclusion mechanism.[30]

In summary, the salt elimination study of the different membranes allowed concluding that, in terms of selectivity, the PCAR2-2%membrane gave the best retention rate of di-monovalent salts, followed by the PCGS membrane (2-2%). However, this retention rate remains insufficient to meet the salinity standards required by the WHO for a concentration of 7.5 g in NaCl.

In conclusion, according to the salt rejection rate, the studied membranes can be ordered in as follows: PCAR2-2% > PCGS2-2% > PCAS2-2% > PCGS2-3% > PCAS2-4% > PCAF2-4% > PCGE2-2% > PCAE2-2%. The PCAR membrane (2-2%) was considered the most reliable and efficient for the elimination of monovalent salts from a selectivity point of view. It presents the optimal characteristics: a flux of 127.37 L/m² h and permeability of 26 L/m^2 h bar, as well as salt retention rates of 34%, 88.3% and 97.3% for NaCl, $CaCO_3$ and $MgSO_4$, respectively. These values show that the different mass transfer parameters obtained for this membrane (PCAR2-2%) correlate with the properties of a NF membrane. The rejection varies inversely with the flux, this is quite logical since the selectivity of the membranes is all the more important as the pores of the membrane are small.

Table 2
Concentrations of Mg^{2+}, Ca^{+2} and NaCl salts and their retention rates

Concentration, mg/L	Ca^{2+}	Mg^{2+}	TH	TR [Ca^{2+}]	TR [Mg^{2+}]	TR [NaCl]
PCAR2-2%	0.16	0.06	0.22	88.3%	97.3%	34.28%
PCAS2-2%	0.25	0.24	0.49	81.2%	89.3%	27.5%
PCAE2-2%	0.26	0.3	0.56	81 %	86.6%	17.2%
PCAS2-4%	0.28	0.29	0.57	79.2%	87%	24.17%
PCAF2-4%	0.40	0.24	0.64	70.4	89.2	21.5%
PCGS2-2%	0.18	0. 266	0.44	86.7%	96.2%	32.17%
PCGE2-2%	0.23	0.234	0.464	82.9%	89.5%	19%
PCGS2-3%	0.20	0.27	0.47	85.5%	87.9%	24.71%
Feed	1.36	2.24	3.6	-	-	-

Table 3
WHO salt standards for freshwater[14]

Salts	Mg^{2+}(mg/L)	Ca^{2+}(mg/L)	NaCl (g/L)
WHO standard	<50	<270	<1

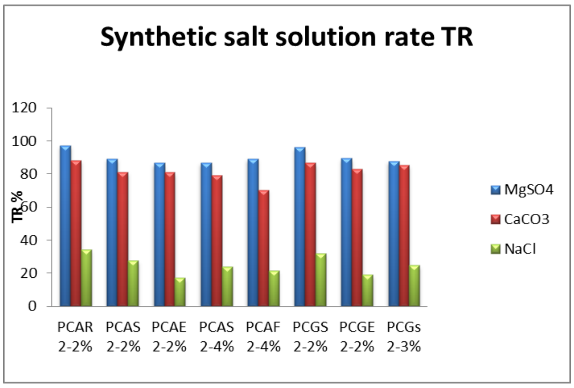


Figure 7: Retention rate (TR) of a synthetic salt solution of $MgSO_4$, $CaCO_3$ and NaCl salts

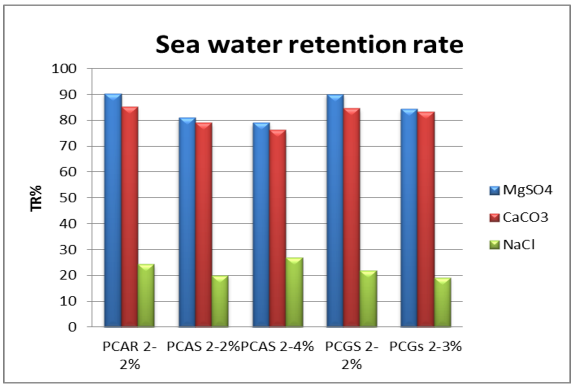


Figure 8: Seawater retention rate (TR) for all membranes

Table 4
Ionic radius, hydrated ionic radius and ion hydration energy[14]

Ion	Ionic radius	Hydrated ionic radius (nm)	Hydration energy (kJ/mol)
Mg^{2+}	0.074	0.429	1921
Ca^{2+}	0.099	0.349	1584
Cl^-	0.181	0.347	515
SO_4^{2-}	0.230	0.380	1138

Study of selective separation for Fouka seawater

The selective salt separation study was conducted for water obtained from real sources, namely, Fouka seawater was used, which is characterized by a pH of 6.9 and a conductivity of 56 mS/cm. The salt separation tests were conducted using the most efficient membranes.

The graph illustrated in Figure 8 shows that the membranes tested are suitable for eliminating between 79-90% of positive divalent Mg^{2+} and Ca^{2+} ions, thus meeting the standards required by the WHO organization. On the other hand, the results remain limited for the elimination of monovalent NaCl salts, thus confirming the findings for synthetic brackish water.[31-32]

It is important to note that the selectivity of a membrane for a given ion is all the more important as this ion is solvated, *i.e.* its hydration energy is high (Table 4). The most hydrated ion hardly crosses the membrane and therefore will be better retained by the membrane.[28] The results of this study led to the conclusion that the sulphate ions were significantly eliminated (Mg^{2+}). The comparison of these results with those obtained for ions reconstituted in the laboratory (synthetic waters) reflects different values. This difference is quite logical if the effect of the interaction of the ions on the retention rate is taken into account. Thus, the prepared membranes can be useful for the removal of water hardness and can contribute to the desalination of low concentration brackish water. These results confirm that the retention of monovalent salts is limited by the nanofiltration process.[32]

CONCLUSION

In this research, different coagulation methods were applied to prepare CMC-x/Psf thin film membranes. Also, glutaraldehyde (GA) and lactic acid (LA) were applied as crosslinking agents in a solution containing carboxymethylcellulose (CMC). The study examined the influence of all the processing parameters on the efficiency and performance of the membranes obtained. The essential results can be summarized below.

The study of the wettability of the membranes was carried out taking into account the water content parameter and the highest water absorption, of 50%, was obtained for the PCAR 2-2% membrane. This can be explained by the swelling phenomenon that can occur at the surface of this membrane where the CH_2-OH groups interact with water via van der Waals forces and hydrogen bonds, so that the wettability increases. Also, the developed membranes were examined in terms of flux and rate of rejection. The tests carried out confirmed that the coagulation of the membrane with distilled water followed by the CMC-X solution gives the best flow rate, while the best rejection rate was obtained for the membrane coated with the lactic acid solution (PCAR). The results concerning the rejection of the studied salts revealed that the highest retention rate of the NaCl salts was obtained for the PCAR membrane, but which remains insufficient to meet the salinity standards for freshwater recommended by WHO. Concerning the rejection of the divalent salts Mg^{2+} and Ca^{2+}, the results were very satisfactory for all the membranes.

The PCAR membrane was considered as the most reliable and effective. It presents the optimal parameters, a flux of 127.37 L/m² h and permeability of 26 L/m² h bar, with salt retention rates of 34%, 88.3% and 97.3% in NaCl, $CaCO_3$ and $MgSO_4$, respectively.

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