Seawater desalination by nanofiltration. increase of productivity by surface modification of membrane

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ABSTRACT

Seawater desalination by membranes has increased in recent years in response to water scarcity and by the development of new nanomaterials. Our research group has developed and patented in Chile a scalable desalination process that considers two stages of nanofiltration in portable units, flexible in capacity, with renewable energy supply and with the possibility of remote monitoring to treat brackish or sea water. The optimization of the operational conditions has allowed the installation of nanofiltration units for the supply of drinking water in coastal communities. In order to improve and contribute to solving the problem of persistent fouling and low productivity, the modification of the surface of the nanofiltration membrane (NF) through the polymerization of pyrrole with the doping of different oxidizing agents has been explored in order to modify the properties of hydrophobicity, roughness, load and permeability.

1. INTRODUCTION

Lack of water resources for consumption and industrial use is one of the greatest concerns worldwide. According to the United Nations Educational, Scientific, and Cultural Organization (UNESCO), it has been estimated that two-thirds of the world's population will be living under water stress by 2025 (Zhao et al., 2018). Methods such as seawater desalination can be used to solve this problem. In fact, desalinated water production has grown rapidly in the past decade, especially in arid coastal zones. The total installed capacity increased by 57% annually between 2008 and 2013, achieving a production level of 80 million m³/day of water in 2013. According to the International Desalination Association (IDA), there were around 16,000 desalination plants in operation in 150 countries by 2015, producing 90 million m³/day of desalinated water (Goh, Lau, Othman, & Ismail, 2018; March, 2015). Desalination costs have dropped by 50% in recent decades as a result of the development of new and modified membranes, and the implementation of energy recovery systems, which make membrane technology increasingly attractive compared to other alternatives (Council, 2008).

Among these technologies, the most attractive is nanofiltration (NF). This technology has stood out above the reverse osmosis, since it is not excessively restrictive to the passage of ions (Mohammad et al., 2015). This feature makes it possible to avoid the need for remineralization post-treatments, causing a 21% reduction in implementation

costs.

In addition, recent research considers the modification of the membrane surface as a promising technique to improve its properties, increasing permeate flux density and salt rejection, reducing the tendency to fouling and improving the removal of micropolutants (Rana & Matsuura, 2010).

2. PROPOSED NANOFILTRATION PROCESS

This dual-stage membrane filtration process developed by Gouellec (Gouellec, 2007) was used as inspiration to implement a flexible system, which allows for easy transport and installation in coastal sectors of Chile (Chilean Patent N^o 52.855, 2013-2033). In fact, the improved NF process presents an adaptable modular system with operational flexibility. Thus, it can be used for seawater and brackish water, which allows obtaining drinking water, or water for a range of industrial and domestic purposes. As it is a flexible modular system of low production, applications of membrane technology to renewable energy generation can also be considered.

In order to develop a pilot system to be installed and operated in the coastal area of the central valley of Chile optimal operating conditions for seawater and brackish water desalination were determined. This included the determination of the best qualities of the obtained permeate, final salt concentration, and permeate flux density. This system was used to demonstrate the technical feasibility of using seawater nanofiltration for producing drinking water that conforms to local regulations (NCh.409), and guidelines of the World Health Organization (WHO).

The implementation of seawater and brackish water desalination processes to produce drinking water is of special interest in Chile due to water scarcity in the dry areas of the country and incidence of droughts. Chile has some of the driest areas in the world. Human activities in these areas require large volumes of water, resulting in high water scarcity that has led to environmental degradation, conflicts and reduced industrial productivity (Aitken, Rivera, Godoy-Faundez, & Holzapfel, 2016). The recent (2010-2015) multi-year, regional-scale dry event has been referred to as the Central Chile mega drought (Boisier, Rondanelli, Garreaud, & Munoz, 2016).

2.1 Nanofiltration process

The system has a capacity to process up to 9 m^3/h of seawater or brackish water. A diagram of the operation using two-stage NF in a series is presented in Fig. 1.



Fig. 1 Diagram of the nanofiltration process

As the system operates continuously, the pretreatment was a microfiltration stage, a stage that involves $FeCl_3$ dosing, and the subsequent removal of precipitates in prefiltering. A prefilter (Clack, model YTP2472–4) filled with commercial "clinoptilolite-zeolite" sand was used for precipitate removal. The MF cut off was 1-µm tubular filters (TwinPure, polyethylene).

Vitec-4000 antiscalant was added continuously to reduce scaling formation. Dosage level was regulated to minimize fouling. After passing through the MF, water turbidity values were lower than the maximum recommended by the manufacturer of the NF90 membrane (DOW Chemical). Therefore, the input water met the quality requirements needed to ensure a safe and stable process.

In order to define the standard of the water produced in the pilot plant, optimal operating conditions in the first stage were determined based on the energy consumption under continuous operation. Afterwards, the variables that allow the greatest possible product flow at the lowest operational cost in the second stage of nanofiltration were also determined based on the specifications of NCh.409 and the WHO guidelines.

During the six months of continuous operation, characteristics of the seawater were maintained constant. Conductivity and pH values of the seawater used in this study are provided in Table 1.

	Parameter	Unit	Result	
	рН	-	7.4 ±0.35	
	Conductivity	µS/cm	51000 ±200	
	Hardness	mg CaCO ₃ /L	8137 ±20	
	TSS	mg/L	13 ±1.5	
	Chloride	mg/L	19350 ±425	
	Sulfate	mg/L	2719 ±416	
	Nitrate	mg/L	<0.023	
	Boron	mg/L	5.48 ±0.07	
	Sodium	mg/L	11080 ±28	
	Magnesium	mg/L	1672 ±5.4	
	Calcium	ma/L	502 ±0.6	

Table 1. Composition of the seawater used in the tests.

Potassium	mg/L	516 ±2.2
Ammonium	µg/L	130 ±14
Carbonate	mg/L	<3.0

In the first stage of nanofiltration, two modules were operated in parallel. Each module consisted of three membranes, each with a 7.6 m² active surface (NF90–4040). The first stage allowed operation at a maximum pressure of 40 bar and was designed to reach a recovery between 20% and 25%. In the second stage of nanofiltration, two modules were operated. Each module consisted of the same type of membranes as in the first stage. The second stage allowed operation at a maximum pressure of 15 bar and was designed to reach a recovery of 70% of permeate from the first stage.



Fig. 2 Effect of pressure on the permeate flow conductivity and energy consumption (E) in the first stage of nanofiltration. Error bars represent 95% confidence interval of three measurements.

As shown in Fig. 2, the transmembrane pressures affect the permeate flux, as it is the motive power for exceeding the osmotic pressure of the system (Gouellec, 2007; Peeva et al., 2004). A pressure of up to 40 bar was used as the maximum operating pressure of the NF90 membranes. The diffusion and convection phenomena produced solute transport through a nanofiltration membrane. The process of convection prevailed over diffusion at greater pressures, thus increasing the permeate flux (Hilal, Al-Zoubi, Mohammad, & Darwish, 2005).

Electrical conductivity was measured at a one-hour interval in triplicate for the different working pressures in the pilot plant. Fig. 2 shows the salt separation obtained in the first stage. It can be observed that the salt concentration of the permeate decreases with an increase in the pressure of the system (Hilal et al., 2005). No concentration polarization effects were observed at pressures near 40 bar, as already described in the literature (Peeva et al., 2004). At high pressures (36–40 bar), the permeate quality obtained with the membrane was within the expected range, and it was similar to that obtained at lower pressures in biologically treated water (Bunani et al., 2013). Moreover, tangential velocity also causes a decrease in electrical conductivity, thus preventing salt from

compacting on the rough membrane and allowing better rejection (Mänttäri, Pihlajamäki, & Nyström, 2002).

Salt rejection in NF₁ was between 91 and 93% for sodium chloride and chloride ions, respectively. Despite the high separation, the chemical analysis revealed that water composition did not comply with the Chilean standard NCh.409 and the WHO guidelines for drinking water quality. Therefore, the second stage of nanofiltration was necessary to achieve the required quality of the product.

The increase in the operating pressure resulted in an increase in the flow of produced water while operating independently in the NF_2 stage. Fig. 3 shows that an increase in the pressure in the second stage of nanofiltration produced an increase in the total water produced by the pilot plant during the continuous operation of the system.

Fig. 3 Effect of pressure on permeate flux density and conductivity in the second stage of nanofiltration. Error bars represent 95% confidence interval of three measurements.

Second-stage NF concentrate was recirculated toward the seawater or brackish water feed because it had low conductivity and turbidity. This recirculation was done in order to dilute fresh seawater or brackish water, increase salt rejection at the first-stage NF, and increase recovery and the use of the total water that entered in the second stage. The product water, which conforms to the local standard NCh.409 for drinking water quality, was produced by partially mixing water generated in the first stage with that generated in the second stage (Table 2).

Table 2. Total monovalent salt rei	ection in the two-stage nanofiltration process.

Sample	TDS (mg/L)	Cl⁻ (mg/L)	NaCI (mg/L)	рН
Feed	35240 ±104	19350 ±287	28150 ±63	7.4 ±0.3
Permeate 1: 40 bar	2230 ±27	1350 ±24	2150 ±15	6.8 ±0.2
Permeate 2: 15 bar (Product water)	122 ±9	72 ±5	119 ±11	6.9 ±0.2
Nch.409 standard	<1500	<400	-	6.5–8.5

WHO standard	<1000	<250	-	6.5–8.5
% First stage rejection	93.65	93.02	91.04	-
% Total rejection	99.65	99.63	99.50	-

Subsequently, the seawater experiments were replicated with the same operating conditions with brackish water (Table 3). The characterization of brackish water indicates low iron content, and a lower salinity range than that of seawater.

Table 3. Composition of the brackish water used in the tests.

Parameter	Unit	Brackish
pН	-	7.4-7.6
Conductivity	µS/cm	29000-33000
Chloride	mg/L	11310
Sulfate	mg/L	1590
Sodium	mg/L	7300
Manganese	mg/L	0.20
Iron	mg/L	0.8
Silicon oxide	mg/L	0.038

If the two alternatives of operation of the plant are compared, it is concluded that the alternative with which it was obtained higher production times corresponds to that which includes a recycle of the flow of rejection. However, this led to higher energy consumption than by operating the plant without recycle and forced membrane work since it was prematurely capped (by concentrating more salt in the inlet water), but it is justified to get more permeated product in the day. The following figure is presented to have a quick comparison between the two alternatives.

Fig. 4 Comparison of the most relevant characteristics between the two operating alternatives evaluated with brackish water.

It is observed that when operating the plant with recycle there was an increase in the ratio consumed energy/cubic meter of water produced, because with that alternative there was a greater duration of operation of the first stage NF_1 , but this change increased the time of production and therefore a greater flow of permeate product. In addition, the overall recovery rate increased by 1.5%.

Fig. 5 shows that the rejection of salts did not present the same percentage value, being more favorable in the operation with seawater. This is only explained by the fact that the brackish water used showed too much colloidal matter at the time of being treated with the NF membranes, which was deposited on the surface of these adding to the polarization by concentration and blocking of pores, reducing their performance.

Fig. 5 Comparison of the percentages of rejection of salt, ion chloride and total solids dissolved between brackish water and seawater

The rejection of total dissolved solids of the first stage NF₁ reached 87.8% for brackish water compared with 93.65% of the rejection with seawater, while the global rejection reached values over 95%, a very acceptable value for classifying water as drinking water despite the lower performance of the membrane.

2.2 Modification membranes

Membrane modifications were performed on a laboratory scale, by means of oxidative polymerization of pyrrole on the surface of the membrane using $FeCI_3 6H_2O$ as an oxidizing agent and in the presence of three agents: methanol, hydrochloric acid and methyl orange. Modifications were analyzed with RAMAN spectroscopy analysis (NT-MDT model NTEGRA Spectra), FTIR-ATR spectroscopy (Omnic 5.2 Nicolet), and SEM microscopy (JEOL JSM-6390LV) (Fig. 6 and Fig. 7).

On the one hand, polypyrrole when polymerized in the presence of methanol acquires a granular spherical shape with an average diameter of 0.32 μ m, while those synthesized

in the presence of HCI reach 0.41 µm. On the other hand, by synthesizing polypyrrole in the presence of methyl orange, a form of polypyrrole nanotubes is acquired.

Fig. 6 NF 90 membranes modified with polypyrrole. a) Membranes b) SEM.

The resulting Raman and FTIR-ATR spectra for the samples coated with polypyrrole are shown in Fig. 7. In the Raman spectra of the membranes coated with polypyrrole, the representative peaks thereof can be noted: 1591, 1383, 1238, 1079, 1055 and 930 cm⁻¹, that are attributed to backbone mode of C=C bonds and inter-ring C-C mode, the inter-ring stretching C-C vibration mode, antisymmetrical C-H in-plane bending vibrations, the C-H in-plane bending vibrations and the ring interplane deformation, respectively. The molecular structures of globular and nanotubular PPy obtained by chemical oxidation are very close each to other and that both PPy differ only in the organization of polymer chains (Trchova & Stejskal, 2018).

Fig. 7 Raman and FTIR-ATR spectra of the modified membranes.

When observing the FTIR-ATR spectrum of the polyamide nanofiltration membrane,

you can see the well-distinguished peaks. On the one hand, when observing the peaks obtained for spherically deposited polypyrrole, the peaks of the NF 90 membrane do not differ greatly, contrary to what happens with the polypyrrole deposited in the form of nanotubes, since in its spectrum still the contribution of the membrane is noted. The foregoing is that the deposited layer that results with the deposition of nanotubes is thinner than that which results with nanospheres of polypyrrole.

The change of isoelectric point of the membranes was analyzed by means of the potential Z (Anton Paar model Surpass). In Fig. 8 it is shown that the isoelectric point of the membrane analyzed with 0.001 M KCI, moves from a pH 3.2 for the unmodified membrane to 3.9, 4.4 and 4.6 for the case of the environment with HCI, methyl orange and methanol, respectively. In addition, it was found that the modified membranes have less load for the entire pH range analyzed.

Fig.8 Zeta potential measurements as a function of pH, for modified membranes

The results of this work demonstrated the success of a modular nanofiltration plant in the treatment of seawater and brackish water, reducing salts by up to 99.6% in two stages. In addition, the modification of the surface of a nanofiltration membrane was achieved by changing its load, functional groups and roughness.

The objective of this study was to modify the active surface of a nanofiltration membrane by an oxidative polymerization of polypyrrole. The next step will be to evaluate and determine the best type of modification for the surface of a nanofiltration membrane in the treatment of seawater and brackish water.

3. CONCLUSIONS

At the plant scale with seawater, a permeate flux density of 21.0 L/m² h with a recovery of 22.5 % for a feed flow of 4.9 m³/h at 40 bar was achieved in the first stage NF₁, while the salt rejection reached 91%. In the second stage NF₂ at 15 bar, the permeate flow

was 51.3 L/m² h, reaching a total system recovery of 24% and a total salt rejection of 99.6%, which complies with the specifications of the Chilean standard NCh.409 and the WHO guidelines. The final permeate contains 118 mg/L of NaCl.

Salt rejection for brackish water reached 86% in the first stage NF₁ and 96% in the second stage NF₂, values lower than those obtained with seawater (99.6%). The complete analysis of the achieved water complies with all the parameters required by the Chilean standard NCh.409 and the WHO guidelines.

The performance of the plant when working with brackish water was lower than when working with seawater, exclusively because when extracted from a deep well it contained too much inorganic load such as silt and colloidal particles.

Regarding the membrane modification, the presence of the agents that were studied determined the final morphology of the polypyrrole. The results of the Raman spectra showed that the molecular structures of the three morphologies are very close.

The analysis of the surface properties of the membrane modified by zeta-potential gave information about the surface chemistry of the oxidative polymerization of pyrrole. For every agents used, a significative change of iso-electric point in the surface chemistry occurred compared to the commercial NF 90. The negative charge decreased with all modification essays. These preliminary results indicate that the magnitude of electrostatic rejection decrease for the modified membranes, but high rejections of cations could be increased with low pH solutions.

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