



Seawater desalination in Mexican Pacific coast by a new technology: use and perspectives

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ABSTRACT

Mexico is a country with problems of water supply in its northern and central territories, as they are semiarid and due to the increase of nonsustainable water use pattern. The major population and productivity activities are located in these areas of the country. Membrane technologies to achieve the elimination of the dissolved ions from seawater or brackish water are some of the most suitable processes to diversify water supply options because of the long coastline that Mexico has: 9,330 km (7,338 km in the Pacific Ocean). Even reverse osmosis using polymeric membranes is the most used technology; ceramic membranes have some advantages as they are chemically and mechanically more resistant and they have a longer life time and less environmental impact once they are discarded; but as their pore size is larger, they are in the range of nanofiltration (NF). The main objective of this research was to evaluate the performance of a new desalination technology using modified ceramic NF membranes with seawater from Mexican Pacific coast. The study was done for one year and the results demonstrated that these modified NF ceramic membranes have a potential scope to be used as a partial desalination of seawater or as the main process to reduce specific ions.

Keywords: Desalination; Membranes technology; Ceramic membranes; Mexico water problem; Seawater

1. Introduction

In many countries, there is a growing scarcity and a consequent demand of fresh water led by lack of sustainable management (overconsumption, pollution, and deforestation), growth of population and individual consumption, and climatic factors (desertification, climate change, and regional differences). In response to the water scarcity, many technological and administrative solutions have been established worldwide.

Desalination is one of them and has become an increasing industry, even though there are still many negative effects, like its high costs, energetic consumption, and environmental impacts. Reverse osmosis (RO) using polymeric membranes has been the most common and growing desalination technology during the last decades [1,2].

Mexico is a typical case of several factors that converge to produce a water scarcity risk situation, not in the overall water availability but in some areas: 77% of population and major part of productivity

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activities—85% gross domestic product (GDP)—are located in northern-central territories of the country which is arid/semiarid and where there is a minor water availability (32% of total). This is enhanced by other factors as overexploitation of groundwater and surface sources, contamination and the global warming that leads to make drier the Mexican northern-central arid zones [3].

In the other hand, Mexico has 9,330 km of coast line—7,338 km of them in the Pacific Ocean—that make desalination a possible alternative to improve fresh water supply. Up to end of twentieth century, in Mexico there were only small desalination plants, mainly for touristic areas. Now, desalination has been increasing and two major desalination plants for domestic water supply have started operations, one more is in construction and there are some other projects for the coming years. All these plants are designed with RO and using polymeric membranes [4].

Many technological developments have emerged worldwide to improve desalination and reduce its negative impacts, like use of alternative energy sources, posttreatment of concentrated brine, and development of new materials. Ceramic membranes, thicker and with larger pores than polymeric ones, are used mainly for ultrafiltration in pretreatment, but there is a big interest in new developments to be used for nanofiltration (NF) as a desalination process for brackish water or as a previous stage in a desalination of seawater [5]. Ceramic membranes have some advantages due to its greater chemical, biological, and thermal stability, longer lifetime, and feasibility to be modified structurally and chemically [6]. These inorganic membranes are investigated alone and in mixed matrix membranes, combined with polymeric membranes and can be used as a desalination process itself or as first step in a hybrid desalination process [7,8].

This work presents a view of Mexico water scarcity current and future situation; the results of using this new technology with modified ceramic membranes impregnated with metals to filtrate seawater and its perspectives for further applications. Water from Mexican Pacific coast was used to evaluate performance during filtration—salts rejection and flux. The methodology includes the following steps:

- Mexican Pacific seawater physicochemical characterization;
- Preparation of Ag/TiO₂ and Pt/TiO₂ ceramic membranes; and
- Performance of a new technology with modified ceramic membranes to desalinate seawater.

2. Water availability in Mexico

2.1. Present situation

In Mexico, approximately 45% of fresh water supply for all uses comes from surface sources, 27% from groundwater aquifers, and the rest is the direct use of rains. However, 70% of domestic and industrial use of water is groundwater which is necessary for 78 millions of inhabitants from the total population. Mexico faces a water scarcity problem that can be explained by three factors [3]:

- (a) Uneven distribution of water. There is a big contrast between the water available zones and population distribution. Mexico can be divided in two big zones: northern-central and southern ones, as shown in Fig. 1. In the first, water availability corresponds to 32% of the country total, but population is 77% and GDP is 85% (that makes a 1,734 m³ per inhabitant per year). Meanwhile in the southern zone, water availability is 68% of the total and just 23% of population and 15% of GDP (13,290 m³ per inhabitant per year). Besides the geographical unevenness, there is a big temporary heterogeneity as 67% of rain falls during June to September, complicating water storage, furthermore considering that it falls mainly in the southern zone—northern-central average year rain drop is around 250 mm while southern is close to 2,000 mm.
- (b) Increasing quality reduction. Contamination has caused that only about 27% of surface water is considered with satisfactory quality. Approximately, 80% of ground water has good quality, and the main cause of degradation is saline intrusion. For the coming years, domestic and industrial pollution control will reach 100%, but due to the overexploiting and reduction in natural pluvial income, an increasing number of aquifers might get degraded by saline intrusion and heavy metal content once its water table reaches fossil water reservoirs.
- (c) Overexploitation and climate change. Water storage has been reduced in the last decades. Nowadays, there are 101 aquifers considered as overexploited, and 60% of the domestic and industrial water of the country depends on them. Deforestation and city growth contributes to the reduction of water table level of aquifers and less storage of surface reservoirs in addition to reduction of rainwater income.

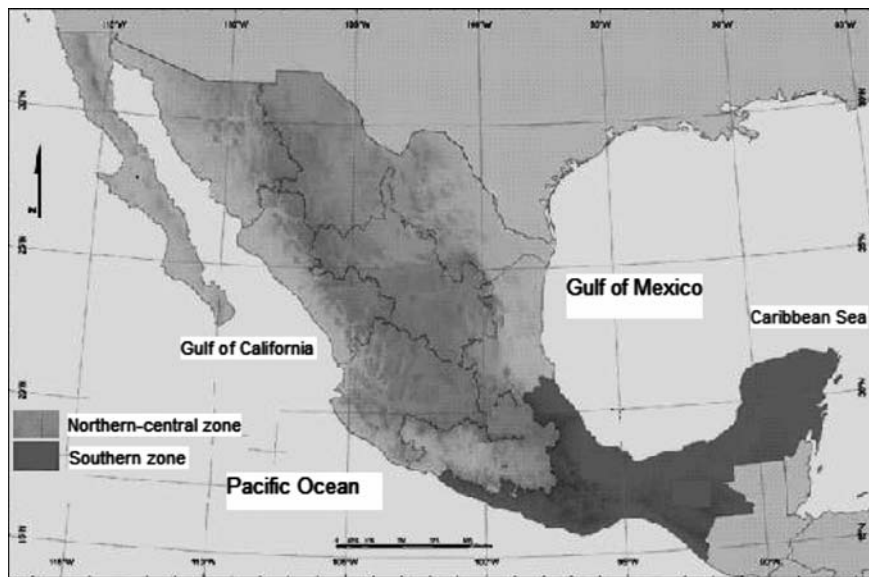


Fig. 1. Water availability zones in Mexico.

2.2. Future situation

In addition to current problems, population and economy growth and climate change might have significant adverse effects.

Water availability in Mexico has been dropping, mainly in the last 40 years and it is estimated that it would continue going down (from 9,645 m³/inhabitant/year in 1970 to 3,783 m³/inhabitant/year in 2030) as shown in Fig. 2.

It is predicted that by 2030, Mexico will need additional 10,000 millions m³ of water, just considering the normal increase of population and economy and taking apart the possible reduction of available water caused by pollution, climate change, and less pluvial income [9].

An increase in 3°C will cause alterations drastically in rainfall, especially in the northern zone and producing more recurrent and intense droughts. In

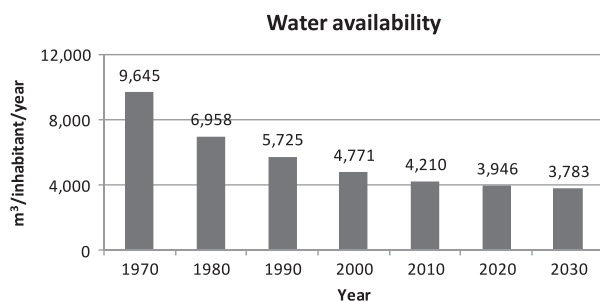


Fig. 2. Decrease and projection of water availability per inhabitant in Mexico from 1970 to 2030.

southern zone, it is predicted that a reduction in overall rainfall and water reservoir level might affect hydroelectrical generation. But tropical storms can be increased in intensity rather than in frequency and more four and five category hurricanes are expected. Sea-level augmentation will propitiate deterioration in Mexican coast and therefore more saline intrusion.

2.3. Desalination in Mexico

Present and future water management requires to overcome these great problems in a global and long-term way. Brackish water and seawater desalination is one of the elements of the total solution to increase water availability.

In past, in Mexico, it was not given the same importance to desalination as in other parts of the world and by beginning of this century there were only small desalination plants, mainly for touristic or industrial use and many of them did not operate regularly because of bad design, maintenance problems, and lack of proper training [4].

Nowadays, in Mexico there are about 500 desalination plants, with an installed capacity of about 200,000 m³/d. Two of them, opened in the last five years are major domestic plants. The plant of Cabo San Lucas (Baja California Sur) is the biggest one, with a capacity of 200 L/s of fresh water; it was opened in 2007. In 2010, the Litibu plant was opened, (in Nayarit state, on Pacific coast) with a capacity of 120 L/s. Now there is another plant under construction in Ensenada (Baja California) with a capacity of

250 L/s; it is expected to open functions in 2013. There are plans for some other desalination plants in the northern zone of Mexico for the coming years.

One of the biggest preoccupations about seawater desalination in Mexico is the environmental risk, as there are many fragile coast ecosystems as mangroves, coralline reefs, and habitats for endemic species or for breeding. Special care and accurate risk evaluation must be done before the installation of a desalination plant, and not considering it as the only solution to freshwater scarcity [10].

3. Ceramic membranes and its use for desalination

RO has become the leading desalination technology since it emerged in the 1970s. Most membranes employed for this technology are polymeric ones. RO consumes around 2–8 kWh/m³ and even it is comparable to the thermal technologies as multiple-effect distillation, it faces some negative effects like its high energy consumption, biofouling, generation of hazardous waste materials and concentrated brine, low resistance to some chemical agents, and loss of flux properties after certain operation time [1,2].

NF can be used to desalinate brackish water as well as pretreatment or first step in integrated membrane desalination operation processes. The use of NF has demonstrated its feasibility because it improves RO performance, reduces biological and chemical fouling, energy, and costs, because it minimizes particulate, bacteria, hardness ions and total dissolved solid (TDS) concentration. Polymer membranes are mostly used for these purposes [5,11].

Ceramic membranes are mostly made of alumina, silica, titania (TiO₂), zirconia, zeolites, or combinations of them. They have a larger pore size so in filtration operation, they are used from ultrafiltration to NF. As they have a big chemical and mechanical resistance, longer lifetime, and can be chemically and structurally modified, many researches have been using in different operations. Some studies have been done using ceramic membranes as a pretreatment process in desalination. The water obtained has a very even quality, low concentration of fouling agents, and produces less biological growth in RO operations [6,7].

Some researchers have tested them in desalination operations: zeolite [12], modified zeolite [13], and titania [14–16]. All these works were carried out with low solid concentration solutions. As general conclusions, they have found that the smaller the pore size, the bigger flux loss is gotten—but it is recovered after chemical washing. In some cases, a good salt rejection can be obtained, close to the values of RO, as the

filtration mechanism is affected by the charged ions adsorbed in the pores making a Donnan exclusion, rather the only pore size exclusion. Also, they have concluded that divalent ions have a greater rejection than monovalent ones.

Another use of ceramic materials is the hybrid membranes that use nanoparticles as coating of polymeric membranes, or mixed matrix membranes. Titania, boehmite, and zeolite have been tested. Titania has disinfection and organic decomposition properties that makes it a good antifouling agent or better with silver [6]. Boehmite has also very good antifouling properties [17], zeolite nanoparticles have demonstrated a small increase in salt rejection without flux loss resulting of a surface change in the membrane [18].

4. Experimental section

4.1. Mexican Pacific seawater physicochemical characterization

For this work, seawater from a zone on Mexican Pacific coast was used. The central point is Playa Blanca, Guerrero (17°34'45", 101°27'97" W) and the sampling was extended 80 km along the coastline. Central point is a bay and the extremes are open sea regions. Mixed samples were prepared from this region taking apart the zones with anthropogenic affectations (touristic and urban areas). This area is a suitable place to install a desalination plant, because of its touristic potential.

Field parameters were determined with a Hanna HI 9828 multimeter for pH, conductivity, and temperature. In laboratory, silt density index (SDI), TDS, and main cations and anions were determined like sodium, potassium, magnesium, calcium, chlorides, and sulphates according to Mexican norms. SDI was also determined according to ASTM, D4189-07 standard test method.

Same parameters were determined in two zones where most of Mexican desalination plants are located: northwest Pacific coast (close to Gulf of California) and Caribbean Sea. The points selected were San José del Cabo, Baja California Sur and Holbox, and Quintana Roo. The three sampled points are shown in Fig. 3.

4.2. Preparation of Ag/TiO₂ and Pt/TiO₂ ceramic membranes

For this work, ceramic multilayer membranes from Tami Industries were used. These membranes have an

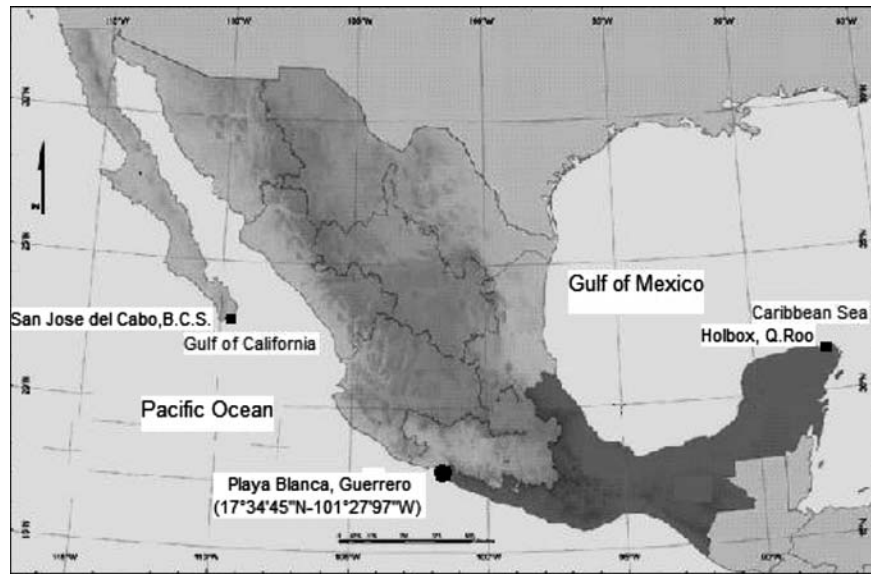


Fig. 3. Location of sampling and seawater characterization zone on Mexican Pacific coast and comparative zones in Gulf of California and Caribbean Sea.

internal layer of TiO_2 —where filtration is made—supported on different layers of $\alpha\text{-Al}_2\text{O}_3$, TiO_2 and ZrO_2 .

The membranes were 250 mm long and 10 mm of outside diameter. Membranes of 5 kD of molecular weight cut off and one channel were employed. Contact surface is 0.0047 m^2 .

The ceramic membranes were modified impregnating them with either platinum or silver. The impregnation was done in solutions of an inorganic salt of the corresponding metal, followed by drying and reduction in tubular oven Barnstead International model F21120–33 (from Thermolyne) according to the methodology explained by Perez et al. [19].

4.3. Performance of a new technology with modified ceramic membranes to desalinate seawater

The modified ceramic membranes were placed in a stainless steel filtration set from Tami Industries, equipped with manometers in the inlet and outlet and seawater passed through the equipment driven by a pump Prominent gamma/ L model 1602 and the operation pressure was six bar. The tested system is shown in Fig. 4.

In the system, desalination tests were carried out with nonmodified and impregnated membranes (with platinum and silver) and seawater was filtered at six bar. Flux was determined and so was the rejection of TDS and some cations and anions.

Flux ($\text{L}/\text{h m}^2$) was determined with the following equation:

$$J = \frac{Q_p}{A} \quad (1)$$

where Q_p is the permeate flow rate and A is the membrane surface.

Rejection of TDS or certain ion, R_i , was calculated using the following equation:

$$R_i = 1 - \frac{C_{p_i}}{C_{f_i}} \quad (2)$$

where C_{p_i} and C_{f_i} are respectively permeate and feed concentration (ppm), of the i ion or TDS.

For comparative reference, in a different equipment, seawater was filtered using RO in an equipment from Prominent using polyamide membrane Desal TFM-50 (from Osmonics). In this case the operation pressure was 10 bar.

5. Results and discussion

5.1. Mexican Pacific seawater physicochemical characterization

Physicochemical parameters of the seawater were determined in Playa Blanca, Guerrero—in Mexican Pacific coast—and compared with two other points, one in San Jose del Cabo close to the Gulf of California, and the other in Holbox in the Caribbean Sea. The results show that the parameters are similar in these zones, with the minimum value in TDS in Playa

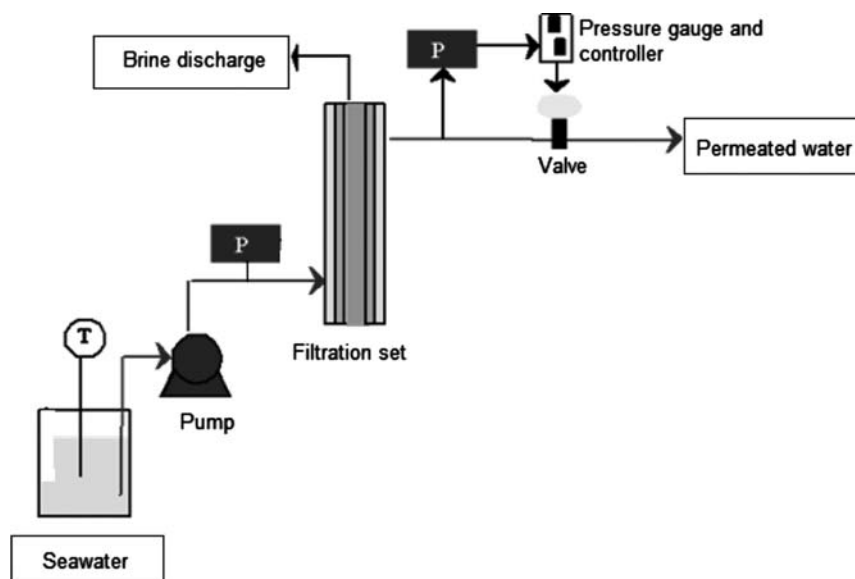


Fig. 4. Diagram of the tested system used for this work.

Blanca; and the same case for SDI. The results are shown in Table 1.

According to the values obtained, the seawater from Playa Blanca might be desalinated by membrane process with a simple pretreatment, as value of SDI is low, using traditional or new technologies.

5.2. Preparation of Ag/TiO₂ and Pt/TiO₂ ceramic membranes

After impregnation and reduction of the metals, the average increase of weight in the membranes is as shown in Table 2.

Table 1
Seawater quality during one year (mean values)

Parameters	Playa Blanca	San Jose del Cabo	Holbox
Temperature (°C)	21.7	20.8	22.7
pH	8.1	8.0	7.9
Conductivity (mS cm ⁻¹)	48.9	55.6	61.3
SDI (% min ⁻¹)	5.0	6.9	9.2
Na ⁺ (mg L ⁻¹)	12,950	13,240	13,790
Cl ⁻ (mg L ⁻¹)	18,650	21,720	22,850
Ca ²⁺ (mg L ⁻¹)	450	320	360
Mg ²⁺ (mg L ⁻¹)	1,490	1,150	1,200
K ⁺ (mg L ⁻¹)	780	320	380
SO ₄ ²⁻ (mg L ⁻¹)	2,630	3,020	3,290
TDS (mg L ⁻¹)	36,750	39,780	41,880

The results are similar when using commercial ceramic membranes like the ones used in this work, but lower when compared with the use of ceramic material in powder and with photochemical deposition or with a coupling agent [20,21]. Metals in general and specially silver can be absorbed in a porous ceramic material but they need to be tightened with a stronger force than the weak van der Waals attraction to avoid being washed away [22]. Platinum, for example, deposits in the inner surface of the pores of TiO₂, when compared with the outer surface.

5.3. Performance of a new technology with modified ceramic membranes to desalinate seawater

Filtration with impregnated membranes had a high flux value when compared with RO; the values are around 80 L/m²-hr as shown in Fig. 5. Operating pressure was considered as inlet pressure, because there was no significant pressure difference between inlet and outlet.

As shown in Fig. 5, flux is good even when the polarization effect of concentrated solution is difficult. The values of ceramic membranes should not be compared directly with the RO membrane, as both types of membranes have a different pore size and operation pressures is different.

When compared impregnated ceramic membranes with nonimpregnated membranes, there is a significant increase in TDS rejection. TDS rejection with ceramic membrane is about 5%, whilst platinum-impregnated ceramic membrane is 22% and

silver-impregnated one is 29%. There is a slightly greater effect with silver impregnation than platinum. The effect of each metal, the difference in the rejection of TDS with metal minus the rejection without metal, is shown in Table 3.

When filtering seawater with impregnated membranes, there is a different behavior between individual monovalent and divalent ions rejection and with the different membranes employed, as it is presented in the following figures and discussions.

In the case of monovalent ions as chloride, there is a similar rejection of about 30% for both impregnated ceramic membranes, with a permeate concentration of 14,000 ppm as shown in Fig. 6. However, the values are far from the value got with RO membrane.

For divalent cations—Ca⁺² and Mg⁺²—rejection values are greater than the ones with monovalent ions. For calcium, there is a similar value with the two impregnated ceramic membranes close to 60%, reaching a permeate concentration lower than 200 ppm as shown in Fig. 7. This is a good rejection value, but it is still smaller than the one obtained with RO membrane.

Table 2
Weight increase of ceramic membranes after metal impregnation

Deposited metal	Number of channels	Weight increase (%)
Platinum	1	0.11
Silver	1	0.12

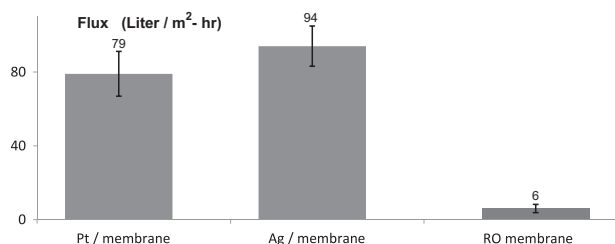


Fig. 5. Mean value of flux with different membranes.

Table 3
Effect of metal impregnation in TDS rejection

Deposited metal	TDS rejection increase (metal effect) (%)
Platinum	17
Silver	24

In the case of magnesium, there is a greater rejection for the platinum-impregnated membrane, over 80%, with a permeate concentration close to 200 ppm. This value, shown in Fig. 8, is very similar to the obtained with the RO membrane. For the silver-impregnated membrane, rejection value is close to 65% with a permeate concentration around 500 ppm.

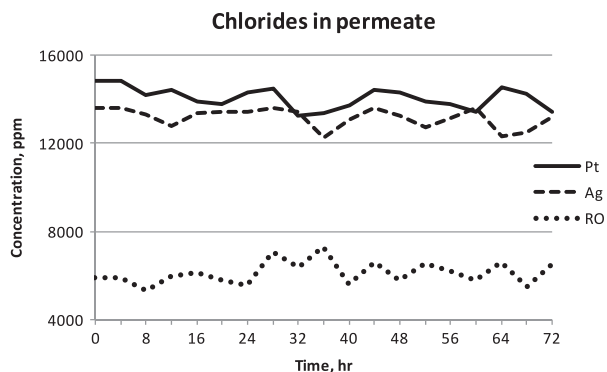


Fig. 6. Chlorides concentration in permeate water for different membranes.

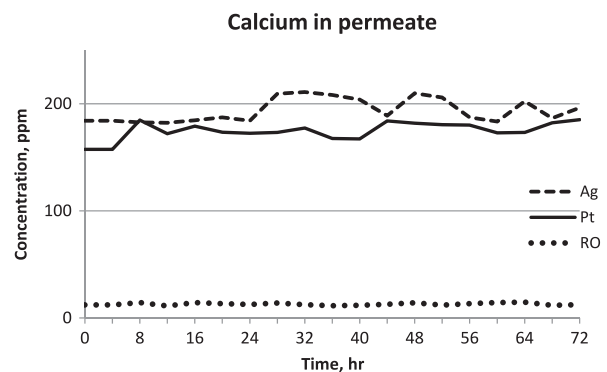


Fig. 7. Calcium concentration in permeate water for different membranes.

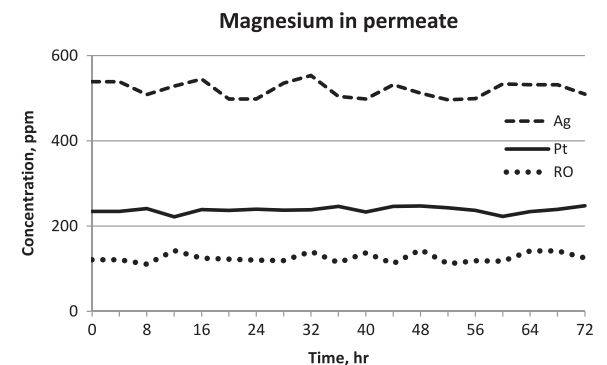


Fig. 8. Magnesium concentration in permeate water for different membranes.

The major divalent ions rejection is coincident with the expected behavior of the metallic membranes because divalent ions, when hydrated, get a longer radius than the monovalent ions. In addition, as the impregnated metals tend to have electropositivity, rejection is greater with cations than with anions. This behavior coincides with the results of other researchers [14–16], for ceramic membranes; however, they used nonimpregnated membranes and low concentration solutions.

5.4. Perspectives of the new proposed technology to desalinate seawater

According to the rejection and flux values, filtration using this new technology with impregnated ceramic membranes has a good potential scope to be used as pretreatment or a previous stage in membrane desalination operations. There are some opportunity areas that need to be explored to complete the results of this research.

Titania, the ceramic material of the membranes tested, has itself antibacterial and antifouling properties ..., which are enhanced by some metals such as silver. Because of that, it is necessary to have a more complete study to verify the potential use of the proposed new technology (titania metal) to inhibit the fouling in RO desalination.

In order to prove the distribution and stability of metallic particles onto the ceramic surface, it is highly recommended to make a characterization of metal-impregnated ceramic membranes, using N₂ adsorption, X-ray diffraction, and electron microscopy—scanning or transmission.

For the application of this new proposed technology, it is recommended to couple it in an integrated membrane desalination process to estimate costs, savings, and escalating problems. There should be savings in the operation, membrane cleaning, and reposition.

As in any new technology, there should be other aspects to be considered like environmental, social, and economical ones and its compatibility with some other technologies.

6. Conclusions

Mexico is facing water scarcity problems that will increase in the coming years, because water availability has been decreasing in the recent years. Seawater desalination is a helpful tool to minimize this problem, together with other solutions and taking care to use the most affordable and environmental-friendly technologies.

The selected place (Playa Blanca), where sampling and characterization were done, in Mexican Pacific coast, is a suitable place to install a desalination plant, according to its touristic potential and the seawater quality after the comparison with two other points.

The new proposed technology, using metal-impregnated ceramic membranes, has shown a good capacity to remove TDS and specific dissolved ions using seawater without affecting flux. Metal impregnation led to an increase of about 20% in TDS rejection when compared with nonimpregnated ceramic membranes. In the case of divalent ions, there was a rejection between 60–80% and in some cases it was close to values obtained with polymeric RO membranes.

There are some opportunity areas that still need to be studied to use the new technology in seawater desalination like the use of it as a pretreatment to reduce TDS, divalent ions, or biofouling in an integrated membrane process or its use in brackish water desalination.

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