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Brackish water desalination using nanofiltration membranes in Morocco

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ABSTRACT

A competing membrane process to reverse osmosis (RO) for brackish water desalination in the near future is nanofiltration (NF). In this work, the possibility of producing drinking water from brackish groundwater (TDS ~ 4 $g.L^{-1}$) using nanofiltration process was investigated. Pilot scale testing was performed in TanTan city (south of Morocco) with a NF/RO pilot-skid system. The performance of commercialized NF membranes (NF90 and NE90) and low-pressure reverse osmosis (BW30) modules was evaluated in terms of water productivity, desalination efficiency and energy requirements. The membrane modules were tested under various operating conditions such as feed pressure and recovery rate. The results showed that NF90 and NE90 membranes are actually better efficient than LPRO since it highly reduced the salinity of Tan Tan brackish water (~ 88% rejection) at higher permeates fluxes, higher recovery rates and lower applied pressures. Surface properties investigation revealed that NE90 membrane is hydrophilic and negatively charged and then can have the best anti-fouling performance. This study confirms the potentialities of NF for brackish water desalination and proved that NF is technically and economically viable to cope with water scarcity and overcome the water deficit in Morocco.

Keywords: Brackish water; Desalination; Nanofiltration; Reverse osmosis

1. Introduction

Reverse osmosis (RO) is recognized as the most energy-efficient desalination process with the greatest number of installations worldwide (60% of installed capacity) [1]. The issue of reducing energy consumption in RO operation has been addressed extensively in recent years. Several recent research studies have evaluated alternate membranes, such as Nanofiltration (NF) membranes to lower the energy requirements associated with RO for seawater and brackish water desalination [2–4]. Nanofiltration, an effective pressure driven membrane process, has the pore size and cut off ability between RO and ultrafiltration. Compared with RO, it operates not only under lower operation pressures and higher water fluxes, but also with high rejection rates [5]. NF had been tried out as one of the pretreatment processes in seawater membrane based and thermal based desalination plant. This resulted in the reduction of TDS in the feed water to RO and multistage flash distiller (MSF) unit [6]. The integration of NF as part of the pre-treatment process also led to a higher water production (around 60%) and resulted in about 30% cost reduction for RO and MSF plants [7]. Recently a novel dual stage NF membrane treatment process was suggested for seawater desalination. Researchers developed two stage NF–NF seawater desalination systems, effectively removing ions from seawater with 20–30% lower energy cost than conventional one-stage RO. It was reported that a fully operational NF–NF process has been established in a facility in Long Beach, USA with

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a daily water production of 1135 m^3 [8]. To date, few studies have been carried out to investigate the possibility of NF to replace or as an alternative approach to RO in brackish water desalination process. Most of these studies have been performed on bench scale using flat-sheet membrane units or dead-end filtration cells [9,10]. In addition, most of these experiments have utilized model feed water such as deionized water spiked with target solutes neglecting water matrix effects on membrane performance. Only a few studies have reported pilot-scale results of NF instead of RO, and only very limited experience exists, both with regards to efficiency as well as water quality. According to these studies the standalone NF process was proved to have a combination of advantages over RO process, such as lower hydraulic pressure, higher rejection, higher recovery rates and lesser flux decline [11–14]. The purpose of this study was to investigate the viability of NF membranes to replace a commonly used RO membrane (BW30) for real brackish water desalination, on a scale that allowed the assessment of operating and water quality conditions representative of full-scale membrane installations. The tradeoffs in choosing low-pressure NF over RO were investigated including whether or not significantly lowering operating pressures/costs would result in diminished permeate water quality. During testing at pilot scale, the performance of different commercial membranes was compared in terms of water productivity, desalination efficiency and specific energy consumption. Characterization of the chemical surface properties of NF/RO membranes through the determination of their surface charge and hydrophilicity/hydrophobicity was also investigated in this study to understand the separation performance of these materials, and to evaluate the fouling propensity of the membranes.

2. Materials and methods

2.1. Membrane surface characterization

Membrane surface charge and hydrophobicity were measured on virgin flat sheets for all membranes used in the field. Prior to membrane characterization, virgin membrane specimens were thoroughly rinsed with ultrapure water and stored at 4°C for 24 h (water was replaced periodically). All samples were stored in a desiccator for 2 d prior to contact angle measurement. The hydrophobicity/hydrophilicity of membranes was characterized by contact angle measurement using a Goniometer (KRUSS G10 USA). For each membrane sample, two specimens were cut from the membrane for duplicate measurement. At least five, 2.0 µL Milli-Q water droplets were applied to the specimen surface and the contact angle was measured immediately after the droplet deposited on the membrane. Contact angle was measured from both sides of the droplet. Membrane surface charge was measured as streaming potential by measuring the difference in electrical potential between both sides of the membrane with a pressure gradient. The streaming potential was measured with two Ag/AgCl electrodes and a piece of membrane (14.5 cm^2 section area) placed in a dead-end filtration cell (Model 8050, Amicon) from Millipore. The streaming potential values were determined in 10^{-3} M KCl solution at pH 8.

2.2. Pilot scale testing

Pilot-scale testing was conducted at a water desalination plant located in the south of Morocco (Tan Tan city) which utilizes brackish groundwater extracted from Khang lahmam aquifer. The raw water is pretreated (acidification, sand filtration, antiscalant injection, microfiltration) prior to being fed to the reverse osmosis trains which use DOW membrane systems (BW30-400 modules) at 70% recovery and approximately 24 $L·m^{-2}·h^{-1}$ permeate flux. The pretreated water from the desalination plant (Microfiltration filtrate) served as feed to the pilot unit used in this study. Tan Tan brackish water composition is summarized in Table 1. The tested water has a total dissolved solids (TDS) content of 4000 $mg·L^{-1}$. Beside sodium and chloride, major constituents with concentrations of more than Moroccan and World Health Organization (WHO) guidelines for drinking water were calcium, magnesium and sulfate. Tan Tan water has a very low colloidal fouling potential (silt density index SDI = 0.3) with a good bacteriological quality and a very low organic content (oxydazibility < 3 ppm). The desalination experiments were performed with a NF/RO pilot-skid system supplied by Veolia Water (Anjou Recherche, France). The testing unit (Fig. 1) is composed of three main systems: (i) a feed tank (volume 3 m^3), (ii) a chilling unit for temperature control of feed water (21°C) and (iii) a skid mounted RO/NF membrane unit supporting a 4″ diameter 40″ long spiral-wound module (surface area S = 7.6 m^2). The selected membranes included two NF membranes: NF90 (Dow/Filmtec) and NE90 (Saehan) with one LPRO membrane BW30 (Dow/Filmtec). In the first part of this study, membrane permeability was determined from Eq. (1) by measuring permeate flux under different operating pressure ranged from 2 to 20 bar. During desalination experiments, the pilot unit was operated at a system recovery of 70% and a permeate flux of 26 $L·m^{-2}·h^{-1}$. The system was operated by controlling the applied pressure as a variable to obtain the chosen permeate flux and recovery rate values. Each filtration run was repeated twice with every membrane and lasted about one hour to reach a steady state.

To calculate the water permeability of each membrane, retention (R), recovery rate (Y) and specific energy consumption (SEC), the following relationships were used.

The water permeability is defined by:

$$J_p = A_m(\Delta P - \Delta \pi) \quad (1)$$

Table 1
Tan Tan brackish water composition compared to drinking water guidelines

	Tan Tan water	In Morocco	WHO
TDS (ppm)	4000	1000	600
SO_4^{2-} (ppm)	500	200	200
Ca^{2+} (ppm)	280	< 500	< 270
Mg^{2+} (ppm)	115	100	< 50
Cl^- (ppm)	1349	350	250
Na^+ (ppm)	595	200	200
NO_3^- (ppm)	20	50	50
SDI	0.3–0.4	–	–

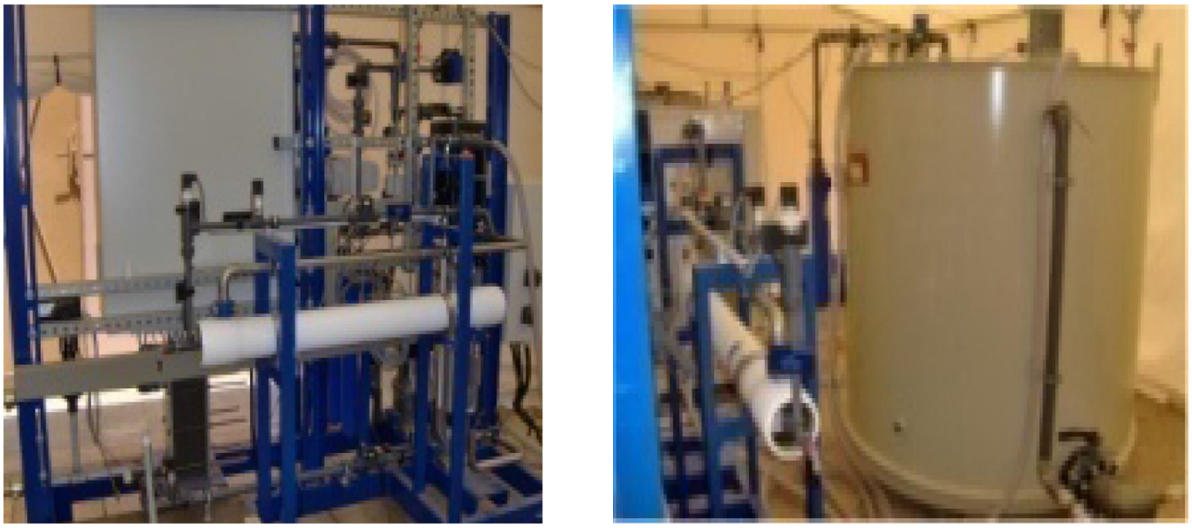

Fig. 1. Image of the RO pilot Skid system.

with J_p is the permeate flux (observed permeate flux divided by membrane area), A_m the membrane permeability, ΔP is the applied pressure and $\Delta\pi$ the osmotic pressure.

The feed water recovery is given by:

$$Y(\%) = \frac{Q_p}{Q_f} \times 100 \quad (2)$$

where Q_p is the permeate flow and Q_f is the feed flow.

The removal of a component of a feed solution is often expressed as rejection which is given as:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

where C_p is the permeate concentration and C_f is the feed concentration.

The pump-membrane energy consumption (SEC) which is proportional to operating pressure can be calculated according to Eq. (4).

$$SEC = \frac{\Delta P}{\eta Y} \times \frac{100}{36} \quad (4)$$

with SEC in $KWh{\cdot}m^{-3}$, ΔP the applied pressure in bar, η is the global pumping system efficiency (80%) and Y the recovery rate.

3. Results and discussion

3.1. Membrane surface characteristics

Performance of RO and NF membranes with respect to both solute separation and permeate flux is mainly governed by the characteristics of the membrane skin layer. Membrane surface characteristics play also a significant role in membrane fouling and scaling for RO/NF desalination systems. Among these characteristics, surface charge and hydrophilicity are reported to be two important factors affecting membrane fouling [15]. Membranes with hydrophilic surfaces often demonstrated less fouling tendency than those with hydrophobic surfaces. Hydrophilic surface tends to resist attachment due to adsorption of organics and such surface is referred as a low fouling surface [16]. In case of surface charge, it has been known that membranes with negative surface charge exhibited low fouling tendency. Most foulants are often negatively charged and, thus, the electrostatic repulsion between charged foulants and membrane surface prevented foulant adhesion. Therefore, the more negatively charged, and more hydrophilic membranes have been considered to be enviable for reducing organic fouling of RO and NF membranes.

Table 2
Surface characteristics of the investigated membranes

Membrane	Contact angle (°)	Streaming potential (mV/bar) pH = 8, KCl 10^{-3} M
BW30	77 ± 5	–4 ± 0.5
NF90	64 ± 2	–18 ± 1
NE90	33 ± 4	–55 ± 3

The membranes under study were characterized for chemical properties such as surface charge and hydrophilicity/hydrophobicity. The results are summarized in Table 2. As shown in this Table, NE90 membrane have hydrophilic surface while NF90 showed medium hydrophobicity. The BW30 membrane have hydrophobic surface. Therefore, NE90 membrane is expected to have the best anti-fouling performance in term of hydrophilicity while BW30 membrane is the worst.

The charge measurement showed a highly negatively charged surface of NE90 membrane in the operating pH (pH = 8). The negative charge on the membrane surface is usually caused by carboxylic acid groups that are deprotonated at neutral pH [17]. Thus, the NE90 membrane is expected to perform well with feed waters containing negatively charged organics and colloids. The streaming potential value of NF90 membrane showed lower negative charge compared to NE90 membrane. For charged organic compounds, electrostatic attraction or repulsion forces between the component and the membrane influence the degree of fouling. A necessary condition for this is that the membrane surface charge is large enough; otherwise hydrophobic forces overcome the electrostatic forces resulting in more fouling of hydrophobic membranes [18]. The BW30 membrane has a relatively neutral surface. This is mainly due to the presence of a neutral polymeric alcohol coating layer onto BW30 membrane [19]. As a result, the NE90 membrane presents a combination of properties like negative surface charge and hydrophilicity that are desirable for long term performance. On the other hand, the BW30 membrane and NF90, to a lesser extent, showed the opposite characteristics and this would contribute to higher fouling behavior. The effect of long term operation under variable flow conditions on membrane desalination performance should also be investigated in future experimental work.

3.2. Membrane permeability

Membrane permeability was measured at first using Tan Tan water as feed. Fig. 2 shows the variation of permeate flux with pressure for all three membranes. Seeing that pressure is the driving force for water permeation, flux increases linearly with increasing pressure (solution-diffusion model) [17,20]. As expected, the permeate flux was higher when operating with NF membranes. It was about three times higher compared to the BW30 membrane at the same pressure, in the range of pressure investigated. NF membrane skin layer with the largest pores are more affected by increasing pressure and produce higher fluxes. The active layer structure of the RO membrane is dense and more compacted and presents very narrow pores; therefore it resists more to pressure changes [21]. The water permeability which was obtained from the slop of the plot is given in Table 3 for each membrane. The water permeability values for NF membranes are more than twice the water permeability of the conventional BWRO membrane. The NF90 and NE90 membrane which have the same molecular weight cut off (MWCO = 200 Da) present different permeabilities. The NF90 membrane which is moderately hydrophobic is more permeable than the hydrophilic NF membrane NE90. A possible explanation is that membrane permeation is also related to surface roughness and to the thickness of the selective layer [17].

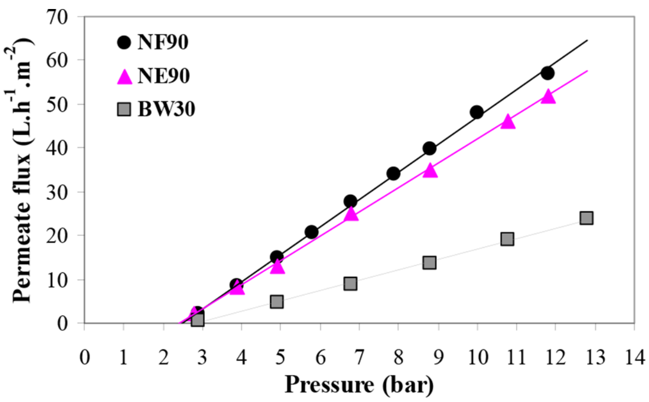

Fig. 2. Permeate flux dependence on applied pressure for the tested membranes (pH = 7.9, T = 21°C, Feed TDS 4 g·L^{-1}).

3.3. Membrane separation performance

The rejection performance of TDS and main ions present in Tan Tan water (SO_4^{2-}, Ca^{2+}, Mg^{2+}, Cl^-, Na^+, NO_3^-) is summarized in Fig. 3. The TDS in the feed water were highly reduced by NF membranes and TDS rejection rates exceed 88%, resulting in a permeate TDS concentrations of 500 mg·L^{-1} on average. For comparison, the BW30 membrane achieved a TDS rejection value of 96%, resulting in a permeate TDS concentration of approximately 165 mg·L^{-1}. The difference in TDS rejection was only 8% between BW30 and NF membranes. The WHO guideline for drinking water is then achieved by NF membranes. Another performance indicator which was examined was the extent of rejection of divalent ions over monovalent ions by NF and RO elements. The BW30 membrane provided greater than 97% rejection of monovalent and divalent ions. This indicates the consistently high performance of BW30 with the dissolved ions in Tan Tan water, and supports that size exclusion is predominant because the BW30 membrane has neutral surface charge [19]. NF90 and NE90 membranes have high rejection rate to divalent ions which exceeds 98%, and significant to low rejection of monovalent ions. This confirms that electrical interactions as well as size exclusion play a role in rejection, as the NF membranes under study are negatively charged [17]. Therefore, divalent ions are more rejected than monovalent ions because charge interactions are larger. The rejection rates of Cl^-, Na^+ and NO_3^- ions from

Table 3
Water permeability (Am) of the investigated membranes

Membrane	Am (L/h·m^2·bar)
BW30	2.4 (± 0.3)
NF90	6.4 (± 0.2)
NE90	5.5 (± 0.2)

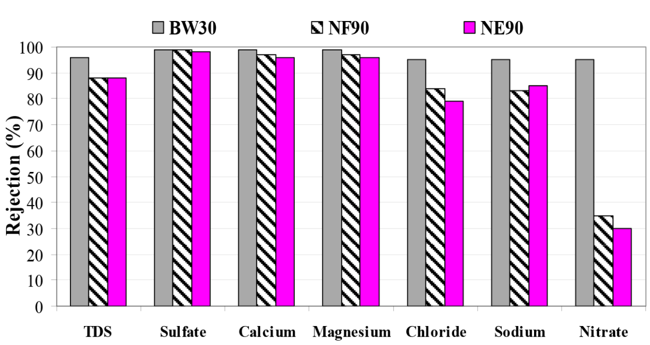

Fig. 3. Average Rejection of TDS and common ions in feed water by the investigated membranes (Y = 70%, permeate flux = 26 L·m^{-2}·h^{-1}, T = 21°C).

feed water with NF membranes were: 85%, 80% and 35% respectively. This is supported because the highest retention is achieved for ions with higher hydrated radii: Sodium (0.358 nm), Chloride (0.335 nm) and Nitrate (0.331 nm) [3]. The low rejection of nitrate by NF 90 (35%) and NE90 (30%) membranes for this application was not an issue as feed concentration was well below the WHO regulation of 50 mg·L^{-1}.

3.4. Working pressures

Besides permeate quality, power consumption is the other important parameter in membrane filtration process. The required working pressures for Tan Tan water desalination at a permeate flux of 26 L·m^{-2}·h^{-1} and a recovery of 70% are presented in Fig. 4. We can see from this figure that the BW30 membrane exhibited a feed pressure of 18 bar while achieving the chosen permeate flux. The NF membranes however required a half of the net driving pressure of the BW30 membrane. This leads to operate at 9 bar maximum when using NF90 and NE90 membranes. The inevitable pump energy consumption for Tan Tan water desalination process was about 0.93 KWh·m^{-3} by RO membrane. While for NF membranes the power consumption was only about 0.44 KWh·m^{-3} and then reduced to half. This is an advantage for NF membranes which are more permeable and require less feed pressures to compensate the resistance to filtration created by osmotic pressure [5]. The BW30 membrane provided the highest rejection rates which results in higher concentration polarization, higher osmotic pressure and consequently lower flux (This directly impacts SEC) [4].

4. Conclution

This pilot study proved the effectiveness of tight NF membranes for desalination of moderately brackish water. It was demonstrated that NF membranes exhibited significantly higher specific flux and revealed that NF90 and NE90 membranes can provide a significant rejection of TDS (88%) at relatively aggressive operating conditions. While the overall ions rejection values are similar for BW30 membrane, the distinction is clearer for the NF90 and NE90 membranes, which is due to the fact that these membranes are selective between monovalent and divalent ions. The suggested NF membranes have also the potential to cut down 50% of the SEC value while providing an acceptable drinking water quality, thus reducing cost demand associated with conventional BWRO desalination process. The membrane's surface characteristics investigation revealed that the NE90 has the best anti-fouling characteristics. But it is difficult to compare and quantify the exact anti-fouling performance of membranes only on the basis of virgin membrane surface characteristics. A more thorough long-term investigation at pilot-scale is required because membrane properties change due to fouling commonly observed in full-scale application.

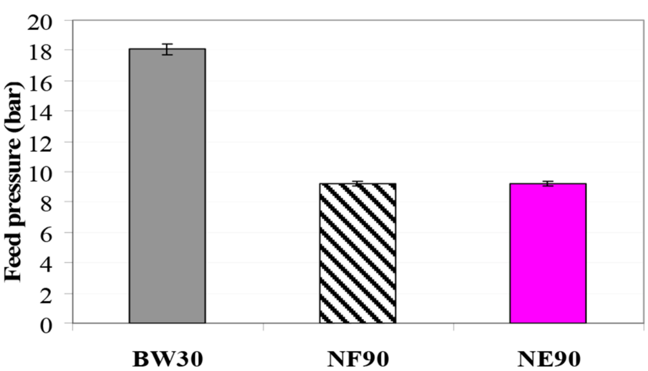

Fig. 4. Feed pressures required for Tan Tan water desalination by the investigated membranes (Y = 70%, permeate flux = 26 L·m^{-2}·h^{-1}, T = 21°C).

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Symbols

ΔP — Trans-membrane pressure, in bar
$\Delta\pi$ — Trans-membrane osmotic pressure, in bar
C_f — The concentrations in the feed solution, in mg/L
C_p — The concentrations in the permeate, in mg/L
Q_p — The permeate flow, in m^3/h
Q_f — The feed flow, in m^3/h
J_p — The permeate flow, in L/h·m^2
A_m — The hydraulic permeability of the membrane, in L/h·m^2·bar
R — The salt rejection, in %
Y — The recovery rate, in %
SEC — The Specifique energy consumption, in KWh·m^{-3}
η — The global pumping system efficiency, in %.

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