Nanofiltration as a sustainable Water Defluoridation operation dedicated to large scale pilot plants for the future

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ABSTRACT

The possibility of producing drinking water from brackish groundwater using nanofiltration (NF) process and the use of this process to remove excess of fluoride ions from brackish drinking water was studied. Brackish groundwater was taken from the south of Morocco (Tan Tan city). The performances of two commercialized spiral wound elements NF and low pressure reverse osmosis (LPRO), denoted respectively NF90 and BW30, were compared. The following parameters hydraulic permeability, total salinity rejection and F- removal were compared under the influence of various experimental conditions such as flow yield, transmembrane pressure and initial fluoride content. Our study showed that the NF90 was actually better efficient vs BW30 since it permits to reduce partially the total salinity of a high fluoride content brackish water with a higher flow yield (70%) and a lower pressure (2 times less).
This study confirms to large scale experiments (membrane surface 7,6 m^2) the performances of NF for a better selective defluoridation of a brackish water opening large perspectives for future large scale nanofiltration units in the world.

KEYWORDS

Water Treatment, Desalination, Defluoridation, Nanofiltration, Reverse osmosis

1. Introduction

Since 1990s, Morocco has resorted to the desalination of brackish water by membrane techniques to supply traditionally deficient regions with good quality water. The desalination plants in Morocco apply the reverse osmosis (RO) process. NF is a concurrent process to RO for the desalination of brackish waters, today 0% of brackish waters market in the world is dedicated to NF, but few projects are in construction and the market is estimated to 10% of the actual RO market in the field of brackish water demineralization.
The nanofiltration membrane (NF) is a type of pressure driven membrane which properties is situated between reverse osmosis (RO) and ultrafiltration (UF) membranes. NF offers several advantages such as low operational pressure, high flux, high retention of multivalent anions salts and biodegradable organic compounds with molecular weight above 300 Da, relatively low investment and low operation and maintenance costs. Because of these advantages, application of NF worldwide has increase. This study contributes to the development of NF technology to produce

affordable drinking water. The aim of this study is to compare the performances; in terms of hydraulic permeability, total salinity rejection and fluoride removal of two membranes (NF90 and BW30) applied to a brackish water from Morocco.

2. Experimental

The experiments were performed on an NF/RO pilot plant supplied by Veolia (Anjou Recherche). The pilot 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 maintained the temperature to 21°C and (iii) a pilot unit which is equipped with one pressure vessel housing on spiral wound module (4”). The membranes used denoted NF90 and BW30, were purchased from Filmtec (DOW, USA) and have a geometrical area of 7.6 m^2. Those membranes are TFC materials (thin film composite) with a skin layer in polyamide. The operations were conducted on a batch mode. The applied pressure was varied from 0 to 20 bar.

Figure 1: Photography of the NF/RO pilot plant

The study was carried out in the place of a brackish water reverse osmosis plant located in Tan Tan city since 2003 (South west of Morocco) equipped with BW30 spiral wound modules (8”) to deliver 150 m^3/h of demineralized water from a brackish water resource which composition is detailed in the Table 1.

Table 1: Characteristics of Tan Tan brackish water with Moroccan and WHO guidelines

	Tan Tan feed water	*Moroccan standards*	**WHO Guidelines**
T(°C)	27	-	**25°C**
pH	7.9	*6.0 - 9.2*	**6.5-8.5**
TDS(ppm)	4010	*1000 - 2000*	**1000**
Cl^-(ppm)	1349	*350 - 750*	**250**
NO_3^-(ppm)	80	*50*	**50**
F^-(ppm)	1.1	*0.7- 1.5*	**1.5**
SO_4^{2-}(ppm)	500	*200*	**200**
Hardness(ppm)	384	*500*	**500**
Na^+(ppm)	595	*200*	**200**

The brackish groundwater samples were collected after sand filtration and antiscalant injection (polyphosphate 3 mg.L^{-1}). Water analysis (Table 1) shows that this water is brackish with high contents of undesirable ions such as C^{l-}, NO_3^-, F^-, SO_4^{2-} and Na^+ in comparison to Moroccan and WHO standards. The Silt density index (SDI) of Tan Tan water has a value of 0.36, which means that this water has a low fouling potential.

The total salinity of the permeate and the raw water was measured with a TDS meter (ECOSCAN TDS6). For F^- ionic selective electrode was used to determine the concentration of fluoride ion concentrations present in the solutions.

3. Results and discussion

3.1 Hydraulic permeability

The interest in measuring the hydraulic permeability of the membranes for Tan Tan water is usable to know the fluxes for the feed brackish water. In the Fig.2, we have reported the flow rate as a function of the transmembrane pressure for Tan Tan water.

As illustrated in the Fig. 2, the NF90 membrane shows a higher hydraulic permeability. Then the permeate flux obtained for the NF membrane is 3 times higher than the BW30 membrane, as usually observed (Pontié *et al.*, 2008). This is mainly due to the larger pore size of the NF90 membrane. Furthermore we obtained from atomic force microscopic analysis a higher roughness for the NF90 membrane (Ra = 298 nm) as we obtained 125 nm for the BW30.Then a higher roughness a higher area exposed to water is observed, as recently reported (Pontie *et al*, 2008).

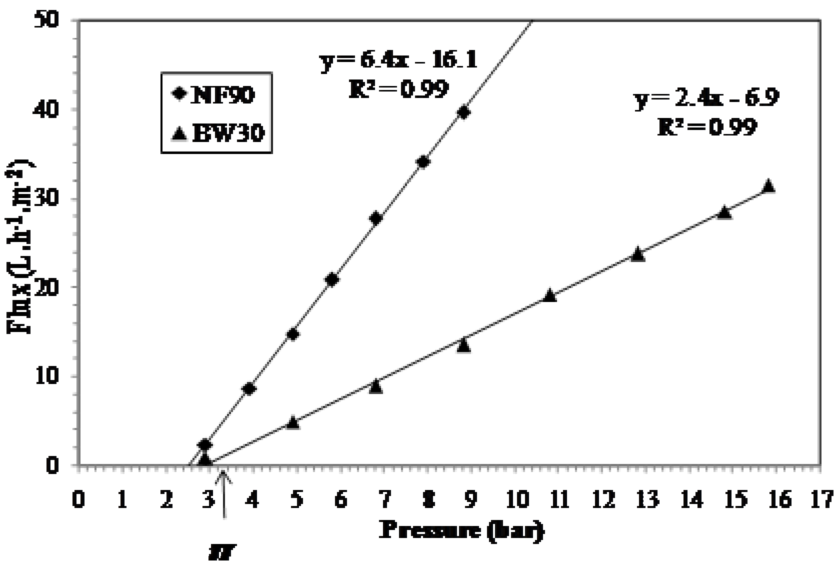

Figure 2: Effect of the applied pressure on Tan Tan water flux for the NF90 and BW30 membranes (pH = 7.9)

The critical driving pressure (Pc), which is defined as the pressure at which the permeate flux is measurable, is observed in NF at 2.5 ± 0.1 bars and 3 ± 0.1 bars for the BW30 in comparison to the theoretical osmotic pressure calculated which is 3.3 bars. Then NF offers the advantage of larger hydraulic permeability correlated to a low effect of the osmotic pressure on P_C vs. LPRO.

3.2 Mass transfer mechanism

The transport of solutes through a membrane can be described by using the principles of irreversible thermodynamics (IT) to relate the fluxes with the forces through phenomenological coefficients. For a two components system, consisting of water and a solute, the IT approach leads to two basic equations:

$$J_v = L_p[\Delta P - \sigma\Delta\Pi] \quad (1)$$

$$J_s = P_s.\Delta C_s + (1-\sigma)J_v C_{int.} \quad (2)$$

where J_v and J_s are respectively the solvent flux and the solute flux, ΔP and $\Delta\Pi$ define respectively the pressure and the osmotic differences between each side of the membrane, *Lp* is the hydraulic permeability to pure water, σ is the local reflection coefficient, P_s is the solute permeability, and $c_{int.}$ is the solute concentration in the membrane and $\Delta Cs = C_m - C_p$ with C_m and C_p the concentrations at the surface of the membrane in the bulk side and in the permeate, respectively. As previously reported (ref) and under steady state the convective and diffusive parts of mass transfer can be separated and explained by the following equation :

$$C_P = \frac{Jdiff}{Jv} + C_{conv} \quad (3)$$

where J_{diff} is the solute flux due to diffusion (with $J_{diff.} = P_M \Delta C_s$), and C_{conv} is the solute concentration due to convection [with $C_{conv} = (1-\sigma)C_{int}$].

The permeate concentration as a function of the reverse permeate flow (figure 3) revealed a linear evolution in conformity to the Eq 3 for the both membranes. The similar behavior of the NF90 vs the BW30 membrane that those membrane due to their diffusional behavior can be good candidates for water defluoridation.

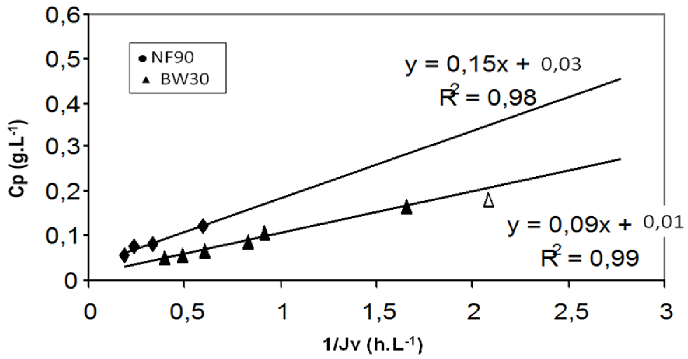

Figure 3 : Permeate concentration Cp vs. he ratio 1/Jv (NaCl 0 .1M, pH=6.8)

3.2 Salt retention

The rejections of the total salinity (TDS) were analyzed as a function of flow yield and reported in the Figure 4. An increase in the flow yield caused an increase of the total salinity in the permeate. Usually the role of the concentration polarization is increasing when the flow yield increase. In NF, a significant decrease of retention with the flow rate was observed. The rejection remains practically constant for the LPRO membrane with the flow yield. If we compare the retentions obtained under the

NF90 and the BW30, we can observe that the NF membrane permits to elaborate water with a total salinity lower than the standards and allows a partial demineralization of Tan Tan water. The rejection rate of the LPRO membrane is extremely low because the membrane is none porous. As usual in RO, a more drastic remineralization step is necessary as a post-treatment.

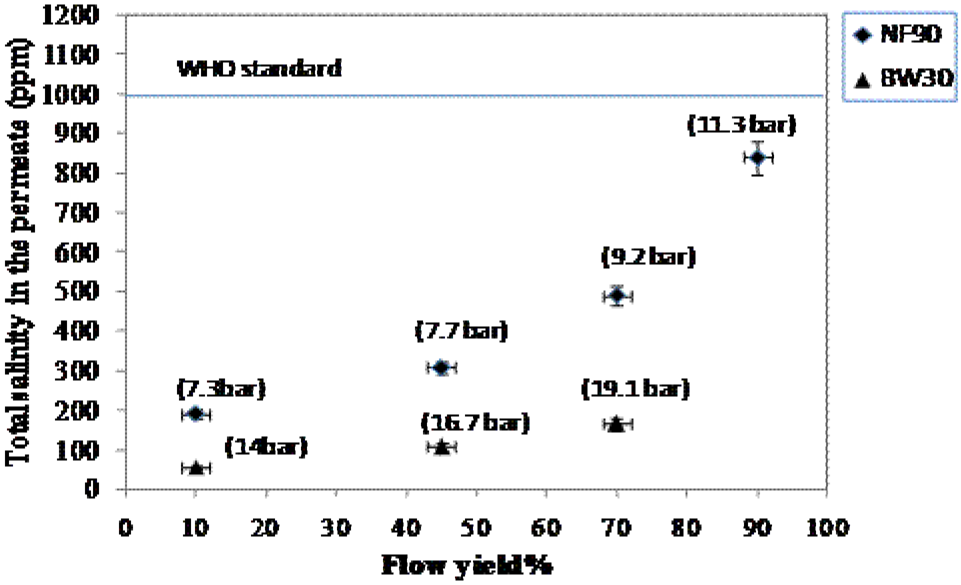

Figure 4: Variations of the total salinity in the permeate as a function of flow yield (pressure applied are detailed into brackets) for the NF90 and BW30 membranes (Permeate flow = 0.2 $m^3.h^{-1}$, pH=7.9)

As waiting, the pressure required to water transport into the BW30 membrane (19.1 bar vs 9.2 bar for a flow yield of 70%) is 2 times higher than the NF90 membrane.

3.3 Defluoridation of brackish water from Tan Tan with high level F^-

Fluorosis, caused by high fluoride intake predominantly through drinking water containing F- concentrations > 2 $mg.L^{-1}$, is a chronic disease manifested by mottling of teeth (dental fluorosis) in mild cases and changes in bone structure, ossification of tendons and ligaments and neurological damage in severe cases (Pontie *et al.*, 1996, 2006). To prevent these adverse effects, the World Health Organization fixed the maximum acceptable concentration of fluoride ions in drinking water to 1.5 $mg.L^{-1}$. The fluoride content in many regions of Morocco greatly exceeds the acceptable standards. For its high and specific membrane selectivity, nanofiltration appears to be the best membrane process to remove fluoride from brackish underground water.

A comparison of the performances of both membranes under study was carried out using various initial fluoride contents in Tan Tan water (doped with NaF at 5, 10 and 15 ppm of fluoride). The flow yield was fixed to 70%. Fig.5 shows the variations of the permeate fluoride concentration as a function of the initial fluoride content.

Practically no influence of the initial fluoride content of the feed water on the fluoride rejection was observed for the BW30 membrane. The fluoride concentration in the permeate is very low and the beneficial effect of fluoride in drinking water (prophylactic good health effect) is not attained due to the fact that fluorides are totally rejected by the BW30 membrane due to the pure solution-diffusion mass transfer mechanism occured in RO (Lhassani et al., 2001). For the NF membrane the fluoride leakage increases with increasing the initial concentration of fluoride.

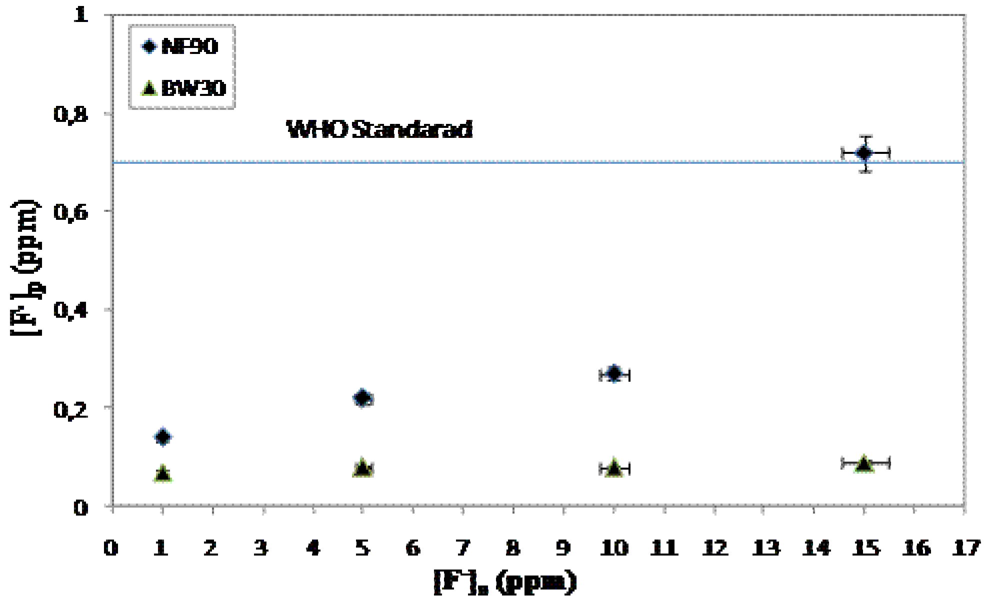

Figure 5: Variations of fluoride concentration in the permeate for the studied membranes with F^- concentrations variations in Tan Tan water (Y= 70%, Permeate flow = 0.2 $m^3.h^{-1}$)

The fluorides were reduced to a satisfactory value; F^- level concentration after filtration, sufficient to maintain a prophylactic benefit effect under dental deases due to the permeate composition (F^- concentration in the permeate around 0.7 mg/L).

4. Conclusion : The possibilities of producing drinking water from high content fluorides brackish water collected from the south of Morocco using NF were studied. NF process was sufficient to obtain in one pass a drinkable water: The TDS of the permeate obtained with this process was inferior to the standard value authorized in Morocco and higher product water fluxes was obtained with a flow yield of 90% for a half time lower pressure in NF90 vs BW30.

This study confirms to large scale experiments (membrane surface 7,6 m^2) the performances of the nanofiltration for a better selective defluoridation of a brackish water opening large perspectives for future large scale nanofiltration units in the world.

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