Performances of nanofiltration and low pressure reverse osmosis membranes for desalination: characterization and modelling

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Abstract. The nanofiltration and the reverse osmosis processes are the most common techniques for the desalination of water contaminated by an excess of salts. In this present study, we were interested in the characterization of commercial, composite and asymmetric membranes of nanofiltration (NF90, NF270) and low pressure reverse osmosis (BW30LE). The two types of characterization that we opted for our study: (i) characterization of electrical proprieties, in terms of the surface charge of various membranes studied by the measurement of the streaming potential, (ii) hydrodynamic characterization in terms of hydraulic permeability with pure water, mass transfer and phenomenological parameters for each system membrane/salt using hydrodynamic approaches. The irreversible thermodynamics allowed us to model the observed retention of salts (NaCl and Na₂SO₄) for the different membranes studied, to understand and to predict a good filtration with a membrane. A study was conducted on the type of mass transfer for each system membrane/salt: convection and diffusion. The results showed that all tested membranes are negatively charged for the solutions at neutral pH, this is explained by their material composition. The results also showed competitiveness between the different types of membranes. In view of that the NF remains effective in terms of selective retention with less energy consumption than LPRO.

Keywords: membrane, nanofiltration, reverse osmosis, streaming potential, mass transfer

1. Introduction
The nanofiltration and the reverse osmosis are the most used techniques for water desalination. The NF membrane is a type of pressure-driven membrane which properties are situated between reverse osmosis (RO) and ultrafiltration (UF) membranes. This positioning of this type of membrane offers advantages, in terms of, low operational pressure, high flux, high retention of multivalent anion salts, relatively low investment and low operation and maintenance costs [1-2].

In order to understand the functioning of membranes, and to make the choice of a membrane for a given application, we have developed two types of characterizations: first (i) characterization of electrical proprieties, in terms of streaming potential and secondly (ii) hydrodynamic characterization, in terms of, the hydraulic permeability, the salts retention, type of mass transfer (diffusion and/or convection).
In this present study, we were interested in the characterization of commercial, composite and asymmetric membranes of nanofiltration (NF270 and NF90) and low pressure reverse osmosis (BW30LE). The composition of the active layer for these membranes is in polyamide, and the support layer is made of polysulfone (Figure 1).

2. Theory

2.1. Streaming potential
The membrane charge into contact with an aqueous electrolyte solution can be determined by the measurement of the streaming potential $SP$ which can be linked to the zeta potential by the equation [3-4-5-6-7]:

$$SP = \frac{\Delta \phi}{\Delta P} = \frac{\varepsilon \zeta}{\mu \chi}$$

(1)

With $\Delta \phi$ is trans-membrane potential difference; $\Delta P$ is the trans-membrane pressure; $\varepsilon$ is the permeability; $\zeta$ is the zeta Potential; $\mu$ is the dynamic viscosity and is $\chi$ he ionic conductivity of the electrolyte solution.

2.2. Hydrodynamic approaches
This approach is based on the irreversible thermodynamics processes [8-9-10]. The equations describe the relationship between the solvent flux and the solute flux which cross through a RO/NF membrane:

$$J_v = L_p (\Delta P - \sigma \Delta \pi)$$

(2)

$$J_s = P_s (C_m - C_p) + (1 - \sigma) J_v C_m$$

(3)

Where $J_v$ and $J_s$ are respectively the solvent flux and the solute flux, $\Delta P$ and $\Delta \pi$ define respectively the pressure and osmotic differences between each side of the membrane, $L_p$ is the hydraulic permeability to pure water, $\sigma$ is the reflection coefficient, $P_s$ is the solute permeability, and the $C_m$ with $C_p$ the concentrations respectively at the surface of the membrane in the bulk side and in the permeate. The observed rejection as reported by some authors may be expressed as [11-12-13-14]:

$$R_{obs} = \frac{1}{(1-\sigma) \exp \left( \frac{J_v}{k} \right) + 1}$$

(4)

Where, $k$ is the mass transfer coefficient.
2.3. Diffusion and convection of salts

In Equation 3, the total flow of salts appears as the sum of diffusion and convection terms [15-16-17]. Thus, it’s possible to write the following equation:

$$C_p = J_{\text{diff}} \frac{1}{J_v} + C_{\text{conv}}$$

(5)

3. Materials and methods

3.1. Streaming potential measurements

The cell is a dead-end cell which has a capacity of 50 ml and used with a flat-sheet membrane. The unit operates at pressure differences using pressurized nitrogen gas as a driving force. Figure 2 shows a schematic representation of the cell which is useful to support membrane samples for the streaming potential measurements.

![Figure 2. Schematic representation of the SP measurement device.](image)

3.2. Laboratory scale filtration unit

A flat sheet laboratory scale NF/RO setup consisting of a planar cross flow module, with a membrane area of 138 cm². The total volume of the system was 5 L. A schematic representation of the equipment is illustrated in Figure 3.

![Figure 3. Schematic representation of NF/RO filtration assembly.](image)
4. Results and discussion

4.1. Characterization of electrical proprieties

As shown in Figure 4, the experience consists to measure the coefficient of streaming potential SP in function of pH.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Streaming potential as a function of pH; KCl $10^{-3}$ M; NF270, NF90 and BW30LE membranes.

In the case of the organic membrane made in polyamide membrane, the amphoteric character of the amino groups of the membrane surface reveals a positive value or a negative value of the streaming potential coefficient SP, according to the pH value [18]. The isoelectric point IEP is the pH value in which the streaming potential coefficient cancels.

| NF/LPRO | NF270 | NF90 | BW30LE |
|---------|-------|------|--------|
| Charge (neutral pH) | Negative | Negative | Negative |
| SP (mV/bar) (KCl $10^{-3}$M; pH = 6.6) | -9.4 | -6.2 | -5.2 |
| IEP (KCl $10^{-3}$M) | 2.6 | 4.4 | 4.9 |

4.2. Hydrodynamic characterization

4.2.1. The hydraulic permeability. The permeability with ultra-pure water (1μs/cm)$L_p$ of investigated membranes is showed in Figure 5.

| NF/LPRO | NF270 | NF90 | BW30LE |
|---------|-------|------|--------|
| $L_p$ ($10^{-6}$ m.s\(^{-1}\).bar\(^{-1}\)) | 1.52 | 1.23 | 1.14 |

The high permeability characteristic generally indicates a high porosity [12]; this is what is observed in the results of the permeability in Table 2 which means that NF270 has the highest porosity and provides a higher permeate flow than NF90 and BW30LE.
4.2.2. Modelling of salts retention. As shown in Table 3, the retention of divalent salts Na$_2$SO$_4$ is higher than monovalent salts NaCl for both type of membrane, this phenomenon can be explained by the hydration energy of salts [6]. The retention of both salts is also dependent of the porosity for each membrane. The experimental data of rejection and flux for all investigated membranes and salts were fitted using the best fit values of $P_\sigma$ and $\sigma$ obtained according to Equation 4. In Figure 6, the modelling showed us that there is a good agreement between experimental and theoretical results. The reflection coefficient $\sigma$ is a characteristic of the convective transport of the solute [13]. For $\sigma$ value of 100% (or 1), mass transfer by convection is totally hindered, it’s the case of BW30LE with both salts and NF90 with Na$_2$SO$_4$ only (Table 4). The results of the permeability of salts $P_s$ decreases initially with the decrease of the pore size of a membrane [19]. The decrease of $P_s$ can also due to the increase of a salt size (or hydration energy of a salt).

Table 3. Retention of NaCl and Na$_2$SO$_4$ salts at three pressures and 10$^{-3}$M of concentration for the NF and LPRO membranes.

| NF/LPRO   | NaCl  | Na$_2$SO$_4$ |
|-----------|-------|--------------|
|           | %Rob of Salts (10$^{-3}$ M) | %Rob of Salts (10$^{-3}$ M) |
|           | P = 4 bar | P = 8 bar | P = 12 bar | P = 4 bar | P = 8 bar | P = 12 bar |
| NF270     | 28.0 | 38.0 | 45.2 | 90.1 | 93.3 | 95.4 |
| NF90      | 30.0 | 45.9 | 61.0 | 93.8 | 95.4 | 96.8 |
| BW30LE    | 74.0 | 80.5 | 85.3 | 94.2 | 95.7 | 98.0 |

Table 4. Phenomenological parameters and mass transfer parameters estimated for NF and LPRO membranes for NaCl and Na$_2$SO$_4$.

| NF/LPRO   | NaCl       | Na$_2$SO$_4$ |
|-----------|------------|--------------|
|           | Salts (10$^{-3}$ M) | Salts (10$^{-3}$ M) |
|           | $\sigma$ ($10^6$ m.s$^{-1}$) | $P_s$ ($10^5$ m.s$^{-1}$) | $C_{conv}$ (g.L$^{-1}$) | $J_{diff}$ ($10^4$ m.s$^{-1}$) | $\sigma$ ($10^6$ m.s$^{-1}$) | $P_s$ ($10^5$ m.s$^{-1}$) | $C_{conv}$ (g.L$^{-1}$) | $J_{diff}$ ($10^4$ m.s$^{-1}$) |
| NF270     | 0.53 | 6.26 | 0.0252 | 0.1165 | 0.96 | 0.343 | 0.0054 | 0.0333 |
| NF90      | 0.87 | 9.62 | 0.0182 | 0.0971 | 0.98 | 0.139 | 0.0018 | 0.0198 |
| BW30LE    | 0.98 | 0.525 | 0.0023 | 0.0250 | 0.99 | 0.111 | 0.0019 | 0.0131 |

4.2.3. Type of mass transfer. In Figure 7 and Figure 8 the plot of $C_p$ vs. $1/J_v$ is linear and the coefficient of determination $R^2$ is very near to 1 which is confirming the relation of Equation 5.
In this experience, we observed that the mass transfer for reverse osmosis membranes is a diffusion type; it’s the case of BW30LE for both salts 

\[ y = 0.1104x + 0.026 \quad R^2 = 0.99 \]

\[ y = 0.0971x + 0.0182 \quad R^2 = 0.98 \]

In nanofiltration membranes, we observe two types of solute transport mode [13], with NaCl is by convection which is a physical nature (Figure 7), and with Na\(_2\)SO\(_4\) is by diffusion which is a chemical nature[20] (Figure 8).

5. Conclusion

The characteristic of electric and hydrodynamic properties which made for commercial and composite membranes showed a competitiveness of NF overlooked LPRO, in terms of, a selective separation of salts (selective desalination), an important hydraulic permeability and lower energy consumption in NF than in LPRO membranes. This study also showed us the functioning and the performance of each membrane studied for a given application.

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Figure 7. Permeate concentration \( C_p \) evolution as a function of the ratio \( 1/J \) for NF and LPRO membranes; ([NaCl]=10\(^{-3}\) M; pH = 6.8; *\( Y = 5\% \); T = 24°C).

*\( Y \): Conversion rate (\( Y\% = (\text{permeate flux/ Total flux})*100 \))
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