

## Performance of Nanofiltration Membranes on Water Demineralization Assessment and Comparative Study

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### ABSTRACT

Ions transport in nanofiltration (NF) membranes was investigated by means of extended Nernst–Planck (ENP) equation and Donnan relationship using as main variables, ions strength, membrane charge density, membrane thickness, and with a permeation flux range of  $10^{-6}$ – $10^{-5}$  m/s. Four different salt solutions were considered: NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaF, and MgSO<sub>4</sub>. Salt rejection coefficient is the main index used for analyzing NF performance for both positive and negative charged membranes. The model calculation showed an excellent agreement with experimental data and high rejection coefficient for Na<sub>2</sub>SO<sub>4</sub> has been obtained. Donnan effect was the major mechanism of rejection for different salt solutions.

**Key words:** Nanofiltration, Membrane, Demineralization, Extended Nernst–Planck.

### 1. INTRODUCTION

Nanofiltration (NF) process has attracted much research on last decade thanks to its amazing features relative to traditionally desalting methods. High salt retention and flux, as well as low investing cost, were predicted for commercial NF membranes.[1-4] Many studies have approved the viability of NF process in water demineralization.[5-8] Hilal *et al.*[9] emphasized that NF membranes (NF90, NF270, and N30F) could achieve 95% rejection of salt exist in brackish water at a pressure of 9 bar, while rejection declined to 41% for solution of 25,000 ppm salt. Tanninen *et al.*[7] applied commercial NF membranes (NF45, NF270, and Desal-5DK) for separation of sulfuric acid from copper sulfate. They found a retention of 96–98% of copper could be obtained at 20 bar for concentrated solution (0.47 M). Hu *et al.*[10] investigated NF membrane (DS-5-DL, DS-51-HL, and SR-1) performance on fluoride removal from high fluoride content water (20–2000 ppm). They found that the rejection of NaF increased with the applied pressure and the solution flux increasing and the feed concentration decreasing. Santafe-Moros *et al.*[8] studied the performance of commercial NF membranes (NF90, NF270 [Dow-FilmTec], and ESNA1-LF [Hydranautics]) in the removal of nitrate ions from aqueous solution. They concluded that the application of the NF technology can be useful to produce drinking water from brackish water with nitrate ion concentration below 150 mg/L.

The aim of this study is to identify the major contributors to solute retention for different NF membranes (NF90, NF270, and N30F). Toward this end, a mathematical model to interpret the membrane behavior is developed. Finally, the model calculations and predictions are compared with the experimental data available in literature. The unique contribution of this study is to discuss various factors to show what additional knowledge of NF behavior can be obtained from more rigorous extended Nernst–Planck (ENP) approach.

### 2. MODEL DEVELOPMENT

The ENP equation has been used to describe the ion transport in NF membranes[11] and RO membranes.[12,13] Mass transfer of charged

solutes across NF membrane pores can be described using the ENP equation:

$$J_i = -K_{i,d} D_{i,\infty} \frac{dc_i^m}{dx} - \frac{z_i c_i^m K_{i,c} D_{i,\infty}}{RT} F \frac{d\psi^m}{dx} + K_{i,c} c_i^m J_v \quad (1)$$

Where,  $J_i$  is the flux of ion (i) based on the membrane area (mol/m<sup>2</sup>.s),  $D_{i,\infty}$  is the hindered diffusivity (m<sup>2</sup>/s),  $c_i$  is the concentration in the membrane (mol/m<sup>3</sup>),  $z_i$  is the valence of ion (i),  $K_{i,c}$  is the hindrance factor for convection inside the membrane,  $J_v$  is the volume flux based on the membrane area (m<sup>3</sup>/m<sup>2</sup>.s),  $R$  is the gas constant (J/mol.K),  $T$  is the absolute temperature (K),  $F$  is Faraday constant (C/mol), and  $\psi$  is the electrical potential (V).[14]

Since the steady-state flux of ion  $J_i$  is  $J_v c_{i,p}$ , where  $c_{i,p}$  is the concentration of the ion in the permeate, the concentration gradient along the membrane pore length can be obtained by rearranging Eq.(1):

$$\frac{dc_i^m}{dx} = \frac{J_v}{K_{i,d} D_{i,\infty}} (K_{i,c} c_i^m - c_{i,p}) - z_i c_i^m \frac{F}{RT} \frac{d\psi^m}{dx} \quad (2)$$

To obtain the potential gradient, the following assumption was implied:

1. The electroneutrality conditions in feed and permeate side:

$$\sum_i z_i c_i = 0 \quad (3)$$

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2. The electroneutrality conditions in the membrane:

$$\sum_i (z_i c_i^m) + z_x c_x^m = 0 \tag{4}$$

3. No electric current is flowing across the membrane

$$\sum_i F z_i J_i = 0 \tag{5}$$

By applying these conditions for equation (2) and rearranging it gives the electrical potential gradient as follows:

$$\frac{d\psi^m}{dx} = \frac{\sum_{i=1}^2 \frac{z_i J_v}{K_{i,d} D_{i,\infty}} (K_{i,c} c_i^m - c_{i,p})}{\frac{F}{RT} \sum_{i=1}^2 (z_i^2 c_i^m)} \tag{6}$$

The distribution of ions between the solution and the membrane is expressed in terms of the effective membrane charge density ( $X_d$ ): [15]

$$\frac{c_B^m}{c_B} = \left( \frac{|z_B| c_B}{|z_B| c_B^m + |z_x| c_x^m} \right)^{|z_B|/|z_A|} \tag{7}$$

The retention ( $R$ ) of ion ( $i$ ) is given as follows:

$$R = 1 - \frac{c_{i,p}}{c_{i,f}}$$

Where,  $C_{i,p}$  and  $C_{i,f}$  are concentrations of ion in feed and permeate side, respectively.

The ENP equation (Eq. 2) combined with Eqs. 3–7 was solved using Runge–Kutta method implemented in Matlab 6.1. To solve these equations, an iterative procedure was used to calculate solute concentration at permeate side.

### 3. RESULTS AND DISCUSSION

#### 3.1. Comparison with Literature

The comparison is made in the case of NaCl salt rejection (Figure 1), using the same operating conditions and membrane characteristics used by Gamze.[16] The calculated rejection coefficient shows a monotonic behavior and good agreement with experimental data. The difference between model and experimental data is very small in the whole concentration range. The most important difference is that in this model the membrane charge density has a constant value, while in actual situation, it continuously increases with concentration. In their analysis, Zerafat *et al.*[17] found that at higher ionic concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub> reduced retention are experienced.

#### 3.2. Concentration Profile of Ions

Figure 2 depicts the Cl<sup>-</sup> concentration profiles calculated at different permeation for negatively charged membrane. The Cl<sup>-</sup> concentration profile is always linear and decreases along the membrane thickness. As permeation increases, lower Cl<sup>-</sup> concentrations are obtained due to the negative effect of the permeation on the Cl<sup>-</sup> transport. At a higher permeation, the electrical potential gradient increases (equation 6) and the ion transport resistance also increases due to the Donnan effect. Other simulations with 1S (single salt solution) for NF membranes report a similar profile with different membrane charges.[8]

#### 3.3. Solutes Rejection

The model calculations and predictions for different types of charged solutes are presented in Figure 3. In general, the rejection is observed to decrease with increasing feed concentration. As seen, the negatively charged membrane followed the salt rejection sequence Na<sub>2</sub>SO<sub>4</sub> > NaF > NaCl > MgSO<sub>4</sub>, which is typical for this type of membrane where Donnan potential plays an important role in its selectivity. Based on ion valence, Donnan exclusion elucidates the salt selectivity sequence observed in Figure 3. For example, R (Na<sub>2</sub>SO<sub>4</sub>) > R (NaCl) because the divalent anion, SO<sub>4</sub><sup>2-</sup>, is strongly rejected by the negatively charged membrane compared to the monovalent anion Cl<sup>-</sup> for the same counterion Na<sup>+</sup>. Similarly, R (Na<sub>2</sub>SO<sub>4</sub>) > R (MgSO<sub>4</sub>) because Donnan exclusion results in stronger attraction of divalent counterions Mg<sup>2+</sup> to the membrane compared to monovalent Na<sup>+</sup> for the same coion SO<sub>4</sub><sup>2-</sup>. To help to understand the membrane rejection behavior, the membrane hindrance coefficient and salt diffusivity are presented in Table 1. With Na<sup>+</sup> as the common monovalent counterion, the negatively charged membrane showed the rejection sequence R (Na<sub>2</sub>SO<sub>4</sub>) > R (NaF) > R (NaCl), which is inversely related to the diffusivity demonstrating the significance of steric effects on its selectivity toward electrolytes with the same valence.

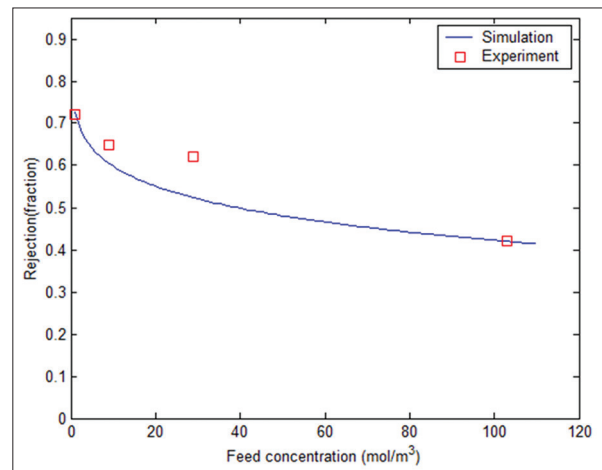


Figure 1: Comparison of rejections of NaCl single salt solution obtained from experiments and performance prediction simulations for NF 270.

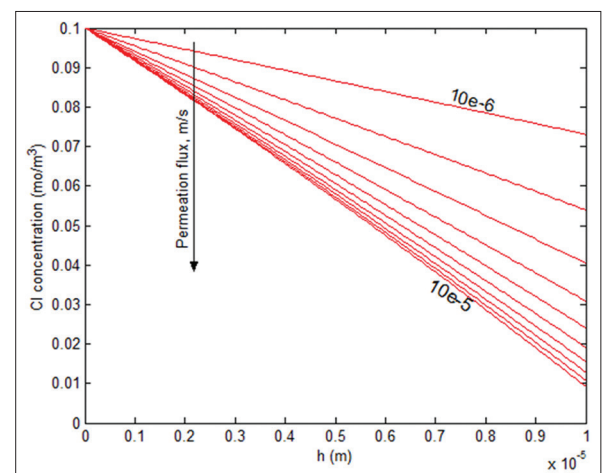


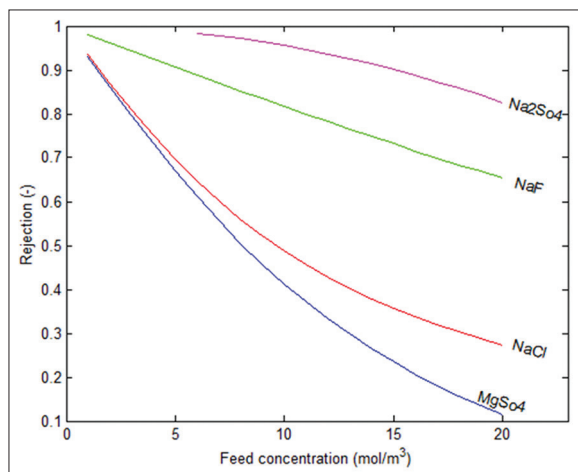
Figure 2: Concentration profiles of Cl ions in negatively charged membrane with NaCl feed concentration of 5 mol/m<sup>3</sup> and fixed charge of -250 mol/m<sup>3</sup>.

### 3.4. Effect of Membrane Charge Density

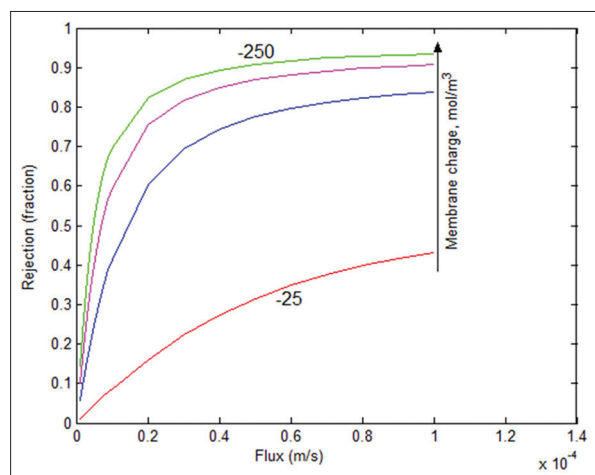
Figure 4 reveals the dual impact of membrane charge density and permeates flux on solute rejection. The constant surface charge density describes the affinity between the charged solutes and the membrane. The NaCl rejection increased significantly (from 0.4 to 0.9) with membrane charge density and permeates flux due to the effect of Donnan potential on membrane-feed side. As membrane charge density increased, the electrostatic repulsion between  $\text{Cl}^{-1}$  ion and membrane also increased results in high solute rejection coefficient. This type of results can be useful to design suitable membrane for treating specific solutions.[8] Similar results were also reported in literature[17,18] and

**Table 1:** Effective diffusivity of solutes

Solute	$K_d$	Diffusivity $\times 10^{-9}$	Effective diffusivity
Na	0.63	1.33	0.873
Cl	0.74	2.03	1.5
Mg	0.34	0.7	0.238
F	0.709	1.46	1.035
$\text{SO}_4$	0.53	1.06	0.561



**Figure 3:** Rejection results for different solutes in negatively charged membrane with flux =  $1 \times 10^{-5}$ , fixed charge =  $-250 \text{ mol/m}^3$ , thickness =  $1 \times 10^{-5}$ .



**Figure 4:** Rejection results for NaCl in negatively charged membrane with feed concentration =  $5 \text{ mol/m}^3$  and membrane thickness =  $1 \times 10^{-5}$  m.

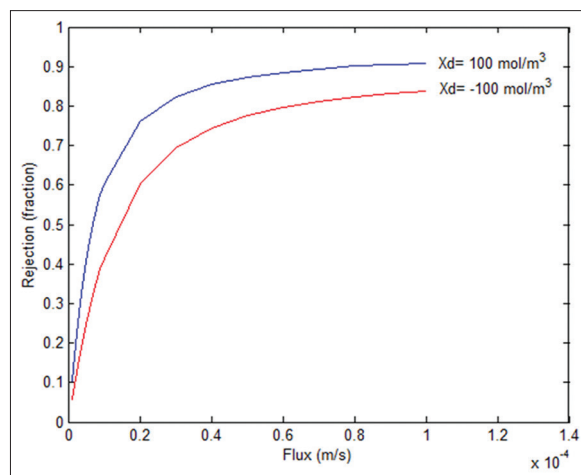
explained that the more negative the charge density of the membrane, the lower the contribution of electromigration, because as the more negatively charged the membrane is the stronger the repulsion of chloride.[19] On the other hand, the higher the charge density of the membrane is the greater the contribution of the diffusive transport.[20]

### 3.5. Effect of Membrane Charge Type

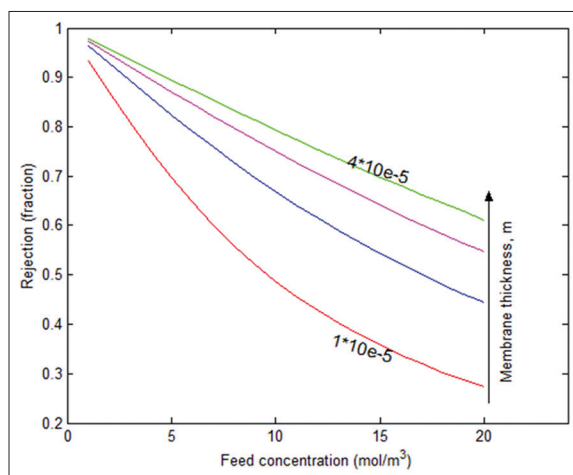
Figure 5 shows the NaCl rejection behavior of membrane with negative and positive charge. It is evident that positively charged membrane has high rejection values with respect to negatively charged membrane due to the high diffusive effect with respect to electromigration effect and also the electroneutrality conditions at bulk phase. Table 1 shows low diffusive coefficient of  $\text{Na}^+$  with respect to  $\text{Cl}^-$  ion ( $1.33 \times 10^{-9}$  and  $2.02 \times 10^{-9}$ ) which is the major factor contributed to high rejection coefficient.[8,14] Has emphasized that a positive membrane charge causes in the one hand a higher concentration of the anion inside the membrane. On the other hand, the positive charge causes a drastic decrease of the cation concentration in the membrane. Inversely, for the case of a negative charge, the anion concentration is lower and the cation concentration is higher.

### 3.6. Effect of Membrane Thickness

The effect of membrane thickness on NaCl rejection is shown in Figure 6. Increasing membrane thickness enhances tremendously



**Figure 5:** Rejection results for NaCl in membrane with thickness =  $1 \times 10^{-5}$  m and feed concentration =  $5 \text{ mol/m}^3$ .



**Figure 6:** Rejection results for NaCl in negatively charged membrane with membrane charge =  $-255 \text{ mol/m}^3$  and permeate flux =  $1 \times 10^{-5}$  m.

solute rejection at high feed solution concentration. This effect can be explained as a result of increasing salt resistance due to high membrane thickness. However, increasing membrane thickness means also low permeate flux and high applied pressure. Therefore, a trade-off between solute rejection and permeate flux should be accomplished. Peeters studied the retention of NaCl using NF45 membrane and found that both a smaller membrane thickness and a lower membrane charge contribute to a lower NaCl retention.[21]

## CONCLUSIONS

The results showed a good agreement between the calculated and experimental rejections for different single salt solutions. The rejection sequence of  $\text{Na}_2\text{SO}_4 > \text{NaF} > \text{NaCl} > \text{MgSO}_4$  was observed which attributed mainly to Donnan effect. On the other hand, diffusive effect played a major effect on high rejection coefficient of NaF with respect to NaCl. High membrane charge density and thickness had a positive impact on ions rejections. High ionic strength decreases ions rejections in contrary to high permeate flux which increases the ions rejections.

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