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# Evaluation of Nanofiltration Processes for Brackish Water Treatment Using the DSPM Model

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## Abstract

Nanofiltration (NF) is a membrane process particularly well suited for the treatment of brackish waters to obtain drinking-water or reuse industrial wastewater. Efficient design of NF systems requires the simulation using mass transfer models to obtain permeate flux and component rejection. The most accurate models depend on feed composition and operating parameters of the system; unlike phenomenological models, these models are difficult to implement because of their complex mathematical structure.

This paper presents an iterative solution of the Donnan-Steric Pore Model (DSPM) and its integration into an overall model to predict NF performance. The developed computer model has shown to be an effective tool to determine suitable NF system configurations and membranes for a particular brackish water problem.

**Keywords:** nanofiltration, simulation, brackish water, DSPM

## 1. Introduction

The growing consumption of water in the southern European countries combined with the industrial and agricultural activities is increasing salinity and pollutant (e.g. nitrates) levels in water. Nanofiltration (NF) membrane processes are better suited for the removal of ions from aqueous solutions with higher permeate fluxes than those obtained by reverse osmosis at the same applied pressure. Therefore, NF can be a good option either to reuse brackish water in many industrial applications or to obtain drinking-water (Van der Bruggen and Vandecasteele, 2003).

The NF modelling is very useful to evaluate the most suitable membrane configurations for a particular water composition. Several models have been developed to model the transport of the different feed components inside the membrane in order to obtain their concentration in the permeate. The phenomenological approaches are not useful for complex ionic mixtures because NF performance is strongly dependent on feed composition. Hence, more accurate models, taking into account charge and steric effects, were developed to predict solute rejection in multi-ionic solutions (Tsuru et al., 1991; Wang et al., 1997; Bowen et al., 1998). In these models, component fluxes and concentration profiles inside the membrane can not be solved independently. Thus, the solving procedure must necessarily be iterative.

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This work presents the implementation of an iterative solution for one of these models known as the Donnan-Steric Pore Model (DSPM), coupled with an approximate description of the concentration polarization phenomena. The procedure used to integrate the differential model for modelling NF systems is explained. The model is very useful for NF process optimization and economic assessment.

## 2. Differential CP – DSPM Model

The task of simultaneously predicting the volumetric flux $J_v$ and component fluxes $J_i$ for a differential membrane area involves a coupled solution of two transport models (Figure 1). The first model describes the concentration polarization (CP) in the feed boundary layer that causes a concentration evolution of each component $i$ from $C_{i,b}$ (bulk) to $C_{i,w1}$ (membrane wall). The second model describes the partitioning of the components between the membrane and the external solutions as well as component transport through the membrane pores (DSPM). The coupling of both models (CP-DSPM) provides the permeate flux and concentrations $C_{i,p}$.

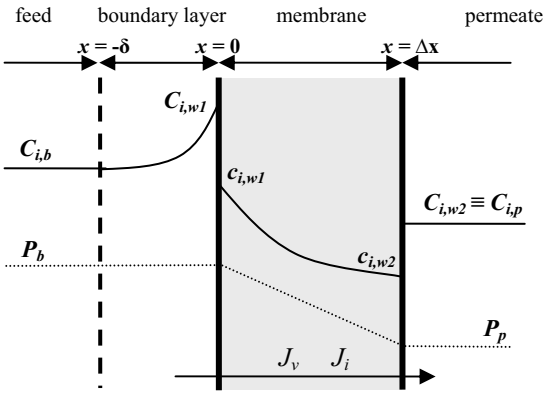


*Figure 1. Mass transfer in a differential element of NF*

### 2.1 Basic equations

The main equations used in the DSPM model are summarized in (1-5) and a complete description can be found in Bowen et al. (1998). The model considers three main parameters: pore radius $r_p$, effective charge density of the membrane $X_d$ and the effective ratio of membrane thickness to porosity $\Delta x/A_k$. Nerst-Planck equation (1) describes the ionic transport through the membrane. The hindered nature of ion transport through the pores is accounted for the ratio $\lambda_i$ of the solute radii to the membrane pore radius that determines the steric hindrance factors $K_{i,d}$ and $K_{i,p}$. The concentration gradient (3) can be obtained combining (1) with the electroneutrality conditions of each solution (2). The relations between the boundary conditions for the concentrations in the membrane and the concentrations in the solutions are established using the Donnan-Steric partitioning equation (4). The volumetric flux $J_v$ is calculated using the Hagen-Poseuille equation (5).

$$J_i = -K_{i,p}\, D_{i,\infty} \frac{dc_i}{dx} - \frac{F\, z_i\, c_i K_{i,p} D_{i,\infty}}{R\, T} \frac{d\psi}{dx} + K_{c,i}\, c_i\, V \tag{1}$$

$$\sum_i z_i C_i = 0 \quad \sum_i z_i c_i + X_d = 0 \tag{2}$$

$$\frac{dc_i}{dx} = J_v \left[ \frac{K_{i,c}\, c_i - C_{i,p}}{K_{i,p}\, D_{i,\infty}} - z_i\, c_i \frac{\sum_i z_i \dfrac{K_{i,c}\, c_i - C_{i,p}}{K_{i,p}\, D_{i,\infty}}}{\sum_i z_i^{\,2}\, c_i} \right] \tag{3}$$

$$\frac{c_{i,w}}{C_{i,w}} = \left(1 - \lambda_i\right)^2 \exp\left( - z_i \frac{F}{R\, T} \Delta\psi_D \right) \tag{4}$$

$$J_v = V\, A_k = \frac{r_p^2}{8\,\mu\left(\Delta x / A_k\right)} \left( \Delta P - \Delta\Pi \right) \tag{5}$$

Concentration polarization in the boundary layer can also be described using Nernst-Planck equation. In this case, the concentration gradients are defined considering the hindrance factors equal to unity. The dependence of the boundary layer thickness δ on cross-flow velocity can be obtained using correlations based on Reynolds and Schmidt numbers (Yang et al, 2003).

## 3. Implementation of the Model Equations

Solution of the coupled model requires to start with guessed $C_{i,p}$ values for each solute (Figure 2). In this way, the ODE sets formed by the concentration gradients can be integrated along the boundary layer and the membrane thickness in order to obtain new $C_{i,p}$ values. In addition, an internal loop is necessary due to the fact that the osmotic pressure difference, and as a consequence $J_v$, depend on $C_{i,w1}$. This value must be recalculated at each iteration step. A fourth order Runge-Kutta method was used to integrate the ODE set. Newton's method was applied to relate membrane wall and external solution concentrations. The problem is equivalent to solving non-linear equation system (6) in which $G$ represents the overall solving procedure of CP-DSPM model providing a new solution vector from the guessed one.

$$F(\vec{x}) = \vec{x} - G(\vec{x}) = 0 \tag{6}$$

Due to the existence of nested loops combined with ODE integrations, the presented problem has a difficult convergence becoming the calculation speed a critical factor. Several iterative procedures were tested. A modified Broyden's method (7) using an approximation of the inverse of the Jacobian matrix $A^{-1}$, eventually proved to be the fastest and most robust method.

$$\vec{x}^{k+1} = \vec{x}^{k} - \alpha \cdot A_k^{-1} \cdot F(\vec{x}^{k}) \tag{7}$$

During the calculation process, parameter α and tolerance values were changed in order to enhance calculation speed or assure the convergence. The implementation of the CP-

DSPM model in MATLAB® v.7 was successfully tested and compared to analytical and experimental results from the literature (Labbez et al., 2002).

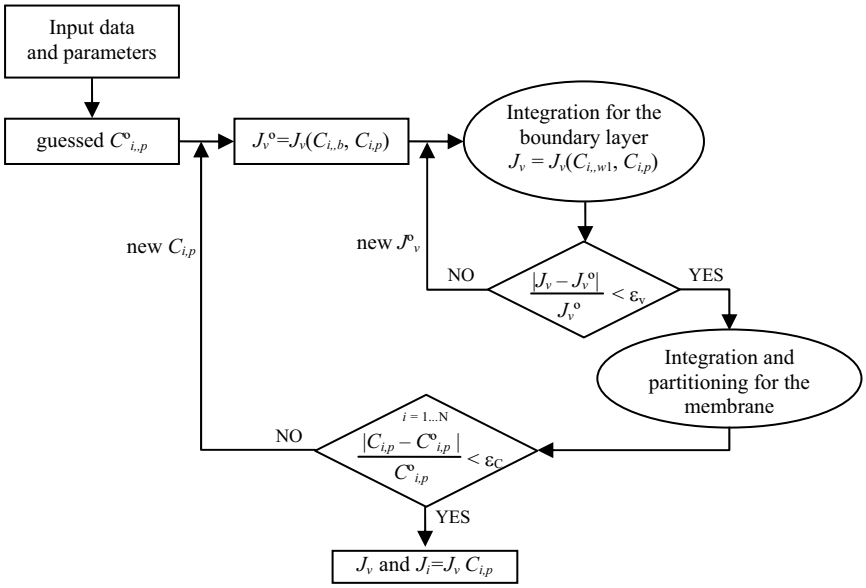


*Figure 2. Basic flow diagram for CP-DSPM*

## 4. Integration of the Differential Model

For the purpose of describing the performance of NF systems, the differential CP-DSPM model was integrated along a coordinate $z$ related to the system length. The differential model provides the solute fluxes as a function of the bulk concentrations, cross flow velocity $v$ and pressure in the feed side. Using the geometric ratio $a$ to express the ratio of membrane perimeter to effective flow section $S$, the mass balance and pressure drop equations can be expressed as:

$$\frac{dv}{dz} = -a\, J_v \tag{8}$$

$$\frac{dC_{i,b}}{dz} = a\frac{-J_i + J_v \cdot C_{i,b}}{v} \tag{9}$$

$$\frac{d\Delta P}{dz} = -h_f(v) \tag{10}$$

An overall balance combined with the ODE integration provides the total permeate flow and the average permeate concentration of the mixture components (Figure 4). These variables represent the product quality and quantity of the system. The stopping criteria were either to have a key component or a TDS over specified limits in the permeate. During the calculation procedure the cross-section of the system was changed to have adequate cross-flow velocity and to avoid excessive concentration polarization (Figure

3). In this way, the change points to a new stage, as well as the membrane area and pumping requirements of the system are obtained, allowing the calculation of the investment and operating costs of the NF installation.

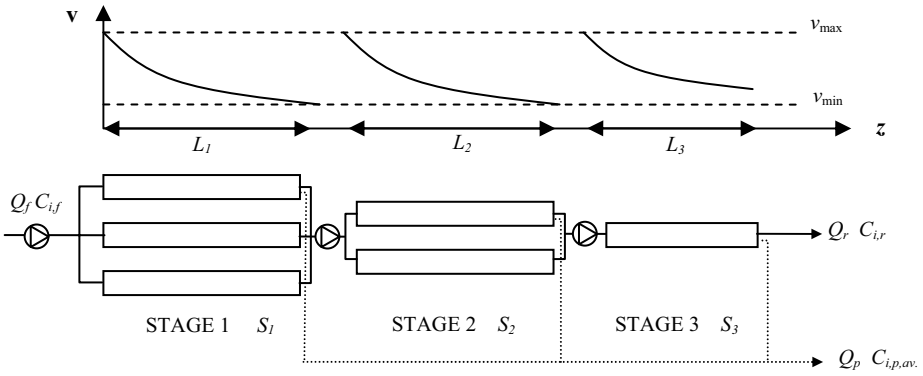


*Figure 3. Section and velocity evolution along z*

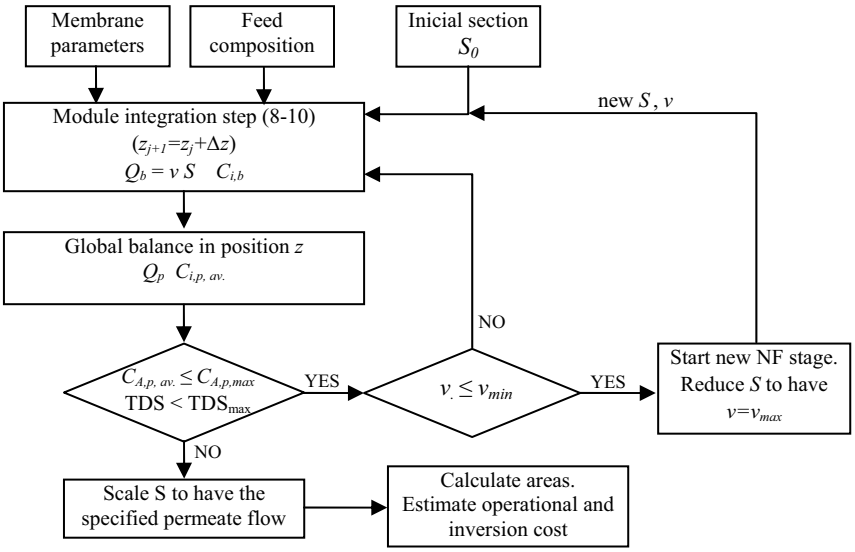


*Figure 4. Basic flow diagram for module integration*

## 5. Case Study: Evaluation of a Brackish Water Treatment

As an example the model was applied to perform a parametric study for the treatment of a feed solution with the following composition in mol·m$^{-3}$: $NO_3^-$=1, $Cl^-$=0.5, $SO_4^{2-}$=4.5, $Na^+$=1.5, $Ca^{2+}$= 4.5. Permeate restrictions for a specified permeate flow were: TDS of 250 ppm and $NO_3^-$concentration less than 35 ppm. In our case, investment and operating costs were estimated using the computed membrane area, pressure profile and entering flow. As shown in Figure 5, the most significant DSPM parameters $r_p$ and $X_d$, determine

the viability regions for the NF systems. Using DSPM values allows us to select the most suitable commercial membranes for a particular type of water. The diagram of Figure 5 provides the guidelines to modify manufacturing characteristics related with the parameters in order to improve performance. For example, larger pore size membranes would require higher charge densities to be effective.

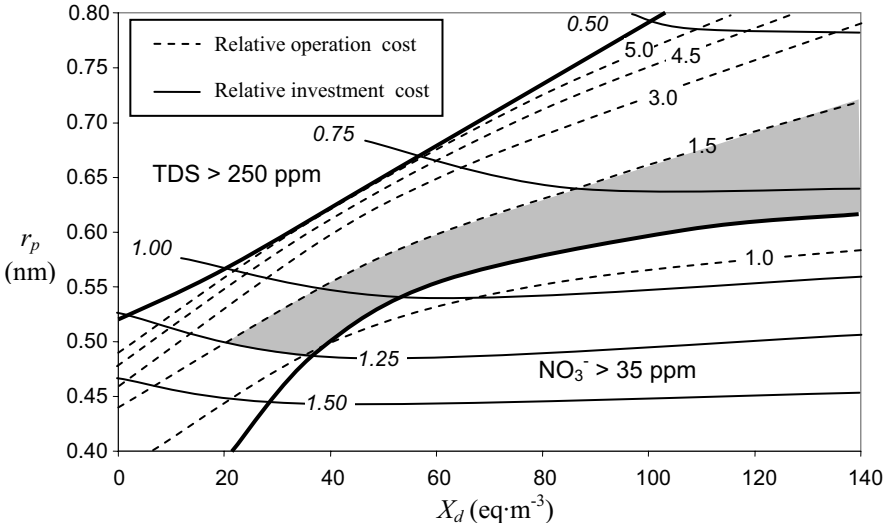


*Figure 5. Relative costs for the brackish water problem referred to typical operation and investment costs for NF installations.*

### 5.1 Numerical results and model validation

The average calculation time for the differential model using MATLAB v.7 in a Pentium IV 3GHz was 2.1 s. The overall model used an integration step size of $dz$ = 0.1 m and employed typically 1 – 2 min in each evaluation. The model was validated by comparing the results with membrane configurations obtained using commercial NF software.

## 6. Conclusions

This paper presents a new approach for NF process design and modelling. The use of MATLAB simplified model software development and data analysis. CP-DSPM model was an effective tool to obtain suitable membrane configurations for the treatment of a specific brackish water problem.

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