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REVIEW

Theoretical performance of nanofiltration membranes for wastewater treatment

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Abstract Mechanisms of ionic transport in nanofiltration are poorly known. Modelling can be used to predict membrane performance, to reveal separation mechanisms, to select appropriate membranes, and to design processes. Several models have been proposed to describe nanofiltration membranes. Some models rely on simple concepts, while other models are more complex and require sophisticated solution techniques. Here, we review predictive models used for characterizing nanofiltration membranes for the separation of wastewater. The most popular model uses the extended Nernst–Planck equation, which describes the ionic transport mechanisms in details. Results obtained by using the extended Nernst–Planck equation show that the performance of nanofiltration membranes is strongly dependent on charge, steric, and dielectric effects.

Keywords Nanofiltration models · Teorell–Mayer–Sievers model · Space charge model · Spiegler–Kedem · Extended Nernst–Planck equation

List of symbols

$\Delta\bar{\varphi}$ Dimensionless membrane potential
 Z_i Electrochemical valence of ions
 X_m Constant volume charged density of charged membrane

D_i Diffusion coefficient of ion
 K_i Partitioning coefficient of ion
 T_r Transmission
 $\zeta_{f(p)}$ Ratio of volume charge density to salt concentration in feed
 T Temperature
 F Faraday constant
 R_g Gas constant
 J_v Volume flux
 J_s Solute flux
 J_i Flux of ion
 I Electric current
 P_0 Effective pressure
 $\Delta\bar{P}_0$ Dimensionless effective pressure
 x Axial distance of the capillary
 Pe Dimensionless Peclet number
 φ Axial component of electric potential
 ν_1 and ν_2 Stoichiometric coefficient of electrolyte
 L_p Pure water permeability
 $\Delta\pi$ Transmembrane pressure
 C_i Concentration of ion
 k_{id} Diffusive hindrance factor
 k_{ic} Convective hindrance factor
 μ_i Electrochemical potential
 a_i Activity coefficient
 $\Delta\bar{\varphi}_{SC}$ Dimensionless membrane potential
 χ_d Membrane volumetric charge density
 η_0 Bulk diffusivity
 β_i Dimensionless quantity
 D_{ip} Pore diffusion coefficient
 $D_{i\infty}$ Diffusivity of species i in water at infinite dilution
 ε_p and ε_b Dimensionless pore and bulk dielectric constants, respectively

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ε^*	Dielectric constant
ΔW_i	Solvation energy barrier
ψ	Electrical potential in the membrane

Introduction

Nanofiltration membranes have recently gain importance in the selective separation of multivalent ions. Nanofiltration membranes are pressure-driven membrane process used in the separation of dissolved components with molecular weight cut off of about 200–1,000 Da and a molecular size of 1 nm (Hassan et al. 2008; Van der Bruggen and Vandecasteele 2003). Nanofiltration process is a complex process at fundamental level. The ionic transport mechanisms and the selectivity of nanofiltration membranes depend on three effects; (1) charge (Donnan effect), (2) steric, and (3) dielectric effects. The nature of the membrane and electrolytes are responsible for the first effect i.e., charge polarities between membrane and the solutes, the second effect is caused by the relative size of ions to the membrane pores, and the third effect is caused by the differences in dielectric constant between bulk and membrane pores (Van der Bruggen and Vandecasteele 2003). These effects offer a value added to the abilities of the membrane separation, which cover almost all the range of liquid–liquid separation system. It has been shown in subsequent investigation that the selection of suitable membrane characteristics for specific processes will give rise to high efficiency and improvement in the process (Bowen et al. 1997). Hence, the dependence of the above listed effects toward rejection behavior should be better clarified in order to produce optimized process parameters that will reduce the cost implication of nanofiltration membranes in industries. Useful models for predicting the performance of nanofiltration membrane separation processes make use of available property data, such as membrane thickness, pore radius, and electrical parameters e.g., the surface charge density and the volumetric charge density (Bowen et al. 1997). It is therefore important to develop a predictive mathematical model in order to characterize membrane in terms of parameters that would be useful in the predictive models.

The simulation of nanofiltration processes in order to design, analyze, and optimize the membrane systems requires suitable model-based process simulation tools (Moros et al. 2008). Some useful models, such as irreversible thermodynamic model and transport mechanism model have been proposed in modelling the rejection performance of salts and charged organics in nanofiltration membranes (Kedem and Katchalsky 1958; Spiegler and Kedem 1966; Levenstein et al. 1996; Schaep et al. 2001;

Mohammad et al. 2007; Murthy and Chaudhari 2009a, b; Sabbaghi et al. 2012). The most cited model that describes the rejection performance of nanofiltration membranes is the Donnan steric-partitioning pore model developed by Bowen and Mukhtar (1996). Donnan steric-partitioning pore model has been applied in some studies (Bowen et al. 1997; Schaep et al. 1999; Gozálviz-Zafrillaa et al. 2005). In this model, Donnan equilibrium and steric effect are responsible for the ionic partitioning between solution and membrane; hence, ionic transport through the membrane is described by extended Nernst–Plank equation and this takes into account electrical potential, diffusion, and convection mechanisms.

The chronology of predictive models development will be discussed; this is important in order to channel the fundamental understanding and the simple quantification of governing phenomena which will be beneficial for industrial application. This review will further cover the inadequacy and adequacy of the different approach of models developed in order to highlight the most accurate and practical model. This will enable the researchers to choose a model that will assist in determining the most convenient transport mechanisms through nanofiltration membranes.

Nanofiltration separation predictive models development

There are two basic approaches in the characterization of nanofiltration membranes: the direct measurement and the analytical methods. By employing mathematical models that have been developed on the basis of transport mechanisms through the porous membrane, the direct measurement methods involve the characterization of nanofiltration membranes using flux and solute data. These are in correspondence to the structure, such as membrane thickness, pore size, and pore size distribution. The analytical method involves the fittings of solute rejection data with the mathematical model. For the past three decades, many works have been devoted to developing reliable mathematical models in characterizing the structure and the solute transport through nanofiltration membranes.

Teorell–Mayer–Sievers model

Teorell–Mayer–Sievers model is a rigorous approach that has been widely used to describe membrane electrical properties (in the case of negatively charged membrane) by assuming a uniform radial distribution of fixed charges and mobile species (Hassan et al. 2007). The model was first proposed by Teorell–Mayer and Sievers (Teorell 1935; Sievers and Sievers 1936). Since then, it has been applied

to describe the transport characteristics and electrokinetic phenomena of charged capillaries (Lefebvre et al. 2004; Aleman and Dickson 2004; Zhou et al. 2005). The basic equations for Teorell–Mayer–Sievers model are the Donnan equation for the partition coefficients of ion concentrations at the surface between the membrane and the external solution, the Nernst–Planck equation, and the different electroneutrality conditions for the inside membrane and the external solutions (Shang et al. 2006). Lefebvre et al. (2004) expressed a dimensionless membrane potential as:

$$\Delta\bar{\varphi}_{\text{TMS}} = \frac{1}{z_2} \ln \frac{k_2^{\text{p}}}{k_2^{\text{f}}} + \frac{D_1 - D_2}{z_2 D_2 - z_1 D_1} \ln \left(\frac{T_r k_2^{\text{p}} + t_1 \zeta_{\text{f}}}{k_2^{\text{f}} + t_1 \zeta_{\text{f}}} \right) \quad (1)$$

Here $\Delta\bar{\varphi} = \frac{F\Delta\phi}{R_g T}$, $t_1 = \frac{|z_1|D_1}{|z_1|D_1 + |z_2|D_2}$, $\zeta_{\text{f}} = \frac{|X_{\text{m}}}{|z_1|v_1 c_{\text{f}}}$, $T_r = \frac{c_{\text{p}}}{c_{\text{f}}}$ where $\Delta\bar{\varphi}$ is the dimensionless membrane potential, X_{m} is the constant volume charge density of the charged membrane, z_i , D_i , and k_i are electrochemical valence, diffusion coefficient, and partitioning coefficient of ion, i , respectively. T_r is the transmittance, which denotes the ability of solute to pass through the membrane, and $\zeta_{\text{f}(p)}$ is the ratio of the volume charge density to equivalent salt concentration in the feed side or in the permeate side of the membrane. T is the temperature; F is the Faraday constant, and R_g is the gas constant (Shang et al. 2006).

Teorell–Mayer–Sievers model was adopted by Shang et al. (2006) to evaluate multivalent electrolyte solutions. In order to achieve a good result, Teorell–Mayer–Sievers model was used in conjunction with Cardano formula in order to calculate the Donnan equation analytically for asymmetry electrolyte (1–2, 2–1). In other words, the application of Teorell–Mayer–Sievers alone was limited without the Cardano formula.

Space charge model

In the concept of space charge model, excess electric charge is treated as a continuum of charge distributed over a region of space, either a volume or an area. According to Shang et al. (2006), the space charge model was originally proposed by Morrison Jr and Osterle (1965), Gross and Osterle (1968) as a modification to Teorell–Mayer–Sievers model, and it has been applied to describe electrokinetic phenomena and transport characteristics of charge capillaries (Philip and Wooding 1970; Fair and Osterle 1971; Sasidhar and Ruckensein 1982; Christoforou et al. 1985; Hijnen et al. 1985; Smit 1989). The three important parameters of the space charge model are pore radius, surface charge density of the capillaries, and the electrolyte concentrations. The basic equations of the space charge model are the Nernst–Planck equation for ion transport, the

Poisson–Boltzmann equation for the radial distribution of the electric potential and the ion concentration, and the Navier–Stokes equation for volumetric flow. According to Shang et al. (2006), Wang et al. (1995a, b) employed the basic derivations used by Sasidhar and Ruckensein (1982) and Smit (1989) to present the relationship of three flow models and three relevant driving forces with the following equations:

$$J_V = \frac{r_p^2}{8\mu} \left(-\frac{dP_0}{dx} \right) + \frac{r_p^2 c v_1 K_{12}}{2\mu} \left(-RT \frac{d \ln c}{dx} \right) + \frac{RT \varepsilon_r \varepsilon_0 K_{13}}{z_1 F \mu} \left(\frac{d\varphi}{dx} \right) \quad (2)$$

$$J_1 + J_2 = \frac{v_1 r_p^2 c K_{21}}{8\mu} \left(\frac{dP_0}{dx} \right) + \left[\frac{D_1 v_1 c K'_{22}}{RT} + \frac{v_1^2 r_p^2 c^2 K''_{22}}{2\mu} \right] \left(-RT \frac{d \ln c}{dx} \right) + \left[\frac{z_1 v_1 D_1 F c K'_{23}}{RT} + \frac{v_1 RT \varepsilon_r \varepsilon_0 c K''_{23}}{z_1 F \mu} \right] \left(-\frac{d\varphi}{dx} \right) \quad (3)$$

$$I = \frac{r_p^2 z_1 v_1 F c K_{31}}{8\mu} \left(-\frac{dP_0}{dx} \right) + \left[\frac{D_1 z_1 v_1 F c K'_{32}}{RT} + \frac{z_1 v_1^2 r_p^2 c^2 F K''_{32}}{2\mu} \right] \left(-RT \frac{d \ln c}{dx} \right) + \left[\frac{z_1^2 v_1 D_1 F^2 c K'_{33}}{RT} + \frac{v_1 RT \varepsilon_r \varepsilon_0 c K''_{33}}{\mu} \right] \left(-\frac{d\varphi}{dx} \right) \quad (4)$$

where J_V , $J_1 + J_2$ and I are the total volume flux, solute flux through a capillary, and electric current, respectively. P_0 is the effective pressure, $c(x)$ is the fictitious concentration inside the capillaries, which was mentioned by Sasidhar and Ruckensein (1982), φ is the axial component of the total electric potential, and x corresponds to the axial direction of the capillary. K_{ij} is mathematically equal to K_{ji} irrespective of K_1 and K_2 on the radial location (Gross and Osterle 1968).

When Shang et al. (2006) introduced the dimensionless form and used non-electrical current condition to obtain the dimensionless expressions of three driving forces as follows:

$$\frac{d\bar{P}_0}{d\bar{x}} = \frac{(v_1 + v_2/v_1)J_s^* L_3 - Pe \bar{c} L_1}{(L_2 L_3 - L_1 L_4) \bar{c}} \quad (5)$$

$$\frac{d\bar{c}}{d\bar{x}} = \frac{(v_1 + v_2/v_1)J_s^* L_4 - Pe \bar{c} L_2}{(L_2 L_3 - L_1 L_4) \bar{c}} \quad (6)$$

$$\frac{d\bar{\varphi}}{d\bar{x}} = \frac{(v_1 + v_2/v_1)J_s^* L_6 - Pe \bar{c} L_5}{(L_2 L_3 - L_1 L_4) \bar{c}} \quad (7)$$

J_s^* and Pe are the dimensionless expressions of solute flux and Peclet number through a capillary. \bar{c} is the dimensionless concentration, v_1 and v_2 are the stoichiometric

coefficients of electrolyte, subscript 1 represents counterion, and subscript 2 represents co-ion. K_{ij} and L_{ij} are functions only with respect to concentration after integrating K_i and ψ along the radial direction; K_i and ψ are functions of concentration and radial location. By integrating Eqs. (4–6) from the high concentration side c_f to the low concentration side c_p , through the membrane, they obtained [(Shang et al. 2006):

$$\Delta\bar{\varphi}|_{SC} = \int_1^{C_p/C_f} \frac{(v_1 + v_2/v_1)(J_S^*/Pe)L_6 - \bar{c}L_5 d\bar{c}}{(v_1 + v_2/v_1)(J_S^*/Pe)L_4 - \bar{c}L_2 \bar{c}} \quad (8)$$

$$\begin{aligned} \Delta\bar{P}_0 &= Pe_p - Pe_\pi \\ &= \int_1^{C_p/C_f} \frac{(v_1 + v_2/v_1)(J_S^*/Pe)L_3 - \bar{c}L_1 d\bar{c}}{(v_1 + v_2/v_1)(J_S^*/Pe)L_4 - \bar{c}L_2 \bar{c}} \quad (9) \end{aligned}$$

$\Delta\bar{\varphi}_{SC}$ is the dimensionless membrane potential, $\Delta\bar{P}_0$ is the dimensionless effective pressure, Pe_p is the Peclet number for the Poiseuille flow velocity, computed at the applied pressure drop, and Pe_π denote the Peclet number for the osmotically driven flow in an ideal semi-permeable membrane (Shang et al. 2006). Although a successful nanofiltration prediction by space charges model was reported by Wang et al. (1995a), the application is limited due to the complex calculation requirements, especially in mixed electrolytes solutions. Nowadays, the most prevalent nanofiltration models are derived from space charge model by assuming radial homogeneity of ionic concentration and potential across the pores, which is valid in the case of small surface charge densities and sufficiently narrow pores, maintained under most nanofiltration conditions (Zerfat et al. 2013).

Spiegler and Kedem model

An irreversible thermodynamic model was first derived by Kedem and Katchalsky (1958) and Spiegler and Kedem (1966). In this method, the membrane is treated as a black box by neglecting the porosity of the membrane; detailed solute transport mechanisms can, therefore, not be obtained. The three important parameters of the mechanisms of Spiegler and Kedem model are as follows: hydraulic permeability, solute permeability, and reflection coefficient. Here, volume flux and solute flux rely solely on the driving forces, which are the operating pressure and the osmotic pressure. The derivation of Spiegler and Kedem model expressed the volume and the solute flux across the membrane as:

$$J_V = L_p(\Delta p - \sigma\Delta\pi) \quad (10)$$

$$j_s = -P_s \frac{dc_s}{dx} + (1 - \sigma)c_s J_V \quad (11)$$

J_V is the volume flux, L_p is the pure water permeability, c_s is the logarithm averaged concentration of solute, $\frac{dc_s}{dx}$ is the concentration gradient across the membrane, σ is the reflection coefficient, j_s is the solute flux, and Δp and $\Delta\pi$ are transmembrane pressure and osmotic pressure differences across the membrane, respectively. The reflection coefficient represents the separation capability of the membrane. Integrating Eq. (11) yields an expression of solute rejection:

$$R = \frac{\sigma(1 - F)}{(1 - \sigma F)} = 1 - \frac{C_p}{C_f} \quad (12)$$

$$\text{where, } F = \exp(1 - J_V(1 - \sigma)/P_s) \quad (13)$$

R is the actual rejection value that considers the concentration polarization factor, while C_p and C_f are permeate concentrations of solute and feed, respectively. The water permeability is evaluated by using Eq. (10), assuming the osmotic pressure difference is zero. The logarithm average concentration c_{lf} is used to determine σ and P_s . Equation (11) now becomes:

$$\frac{j_s}{\Delta c} = P + (1 - \sigma)(J_c c_{lm}/\Delta c) \quad (14)$$

where $\Delta c = C_f - C_p$. If a linear correlation is achieved between $j_s/\Delta c$ and $J_V c_{lf}/\Delta c$, then σ and P_s will, respectively, be a slope and the intersection of y-axis. L_p , σ , and P_s parameters are analyzed by using pore theory in order to understand the actual structure of a membrane.

Murthy and Chaudhari (2009a, b) used the working equations of irreversible thermodynamic Spiegler–Kedem model to explain the retention of electrolyte with a charged nanofiltration membrane. This was done by using combined film theory–Spiegler–Kedem model based on irreversible thermodynamics and ion transport model based on the extended Nernst–Planck equation. Boundary layer thickness, enrichment factors, and concentration polarization modulus together with the membrane transport parameters were estimated by using the Levenberg–Marquadt method. The Spiegler–Kedem model has found wide use for the description and analysis of nanofiltration membranes, but a major disadvantage of this model is treating the membrane as a “black box” (Zhang et al. 2012). That is, these models provide no insight into the transport mechanisms of the membrane. As a result, irreversible thermodynamics models are not very useful for optimizing separations based on membrane structure and properties. Again, these models do not adequately describe water flux for some solute systems, especially some dilute organics (with $\pi_F = \pi_P = 0$) that have substantially lowered water fluxes than those described by Eq. (10).

Donnan equilibrium and the extended Nernst–Planck equation

When charge membrane comes in contact with a salt solution, the ions of the opposite sign of the membrane surface charge will achieve membrane concentration higher than the bulk concentration. From another point of view, ions with same charge as the membrane do not accumulate to the membrane surface to a significant extent. This leads to the creation of Donnan potential (Santafé-Moros et al. 2008). Applied pressure in membrane separations forcing water through the membrane will also further create a potential. In order to maintain electroneutrality, both ions are rejected by the membrane. The salt (M_{zy} , Y_{zm}) distribution coefficient (K^*) is given by the following equation (Santafé-Moros et al. 2008):

$$K^* = \left[\frac{C_{ym}}{C_y} \right] = \left[Z_y^{zy} \left(\frac{C_y}{C_m^*} \right)^{zy} \left(\frac{\gamma}{\gamma_m} \right)^{zy+zm} \right]^{1/zy} \quad (15)$$

where z_i represents the charge of species i , while C_y and $C_{y(m)}$ are the concentrations of ions having same and opposite charge of the membrane surface, respectively. γ , γ_m , and C_m^* are activity coefficients and charge capacity of the membrane. Ion rejection (R) by the membrane is represented as follows (Santafé-Moros et al. 2008):

$$R' = I - K^* \quad (16)$$

This model shows that the ion rejection is a function of membrane charge capacity, solute concentration, and ionic charge. However, this model is qualitative in nature and does not consider the effects of diffusive and convective permeations (Santafé-Moros et al. 2008).

The extended Nernst–Planck equation is to be considered a complex equation that uses the ionic diffusion, electric field gradient, and convection of a membrane to solve flux, or the ability of a particular species to pass through the membrane; in a way that flux is equal to the convection minus the diffusion and the electric field gradient. Hence, the equation does not have any relation to the structural mechanistic of the membrane, but the performance of the membrane. Nanofiltration modelling uses the extended Nernst–Planck equation to incorporate the contributions from diffusion, convection, and electrical migration in order to model ion transport across the membrane. Here, the existence of fixed charges in the membrane influences the ion distribution inside the membrane when working with ionic solutions. Figure 1 shows a solute concentration profiles in the membrane and the feed boundary layer. The Donnan steric Pore model and the steric, electric, and dielectric exclusion model are examples of the approaches based on the extended Nernst–Planck equation. These models have been shown to be reasonably

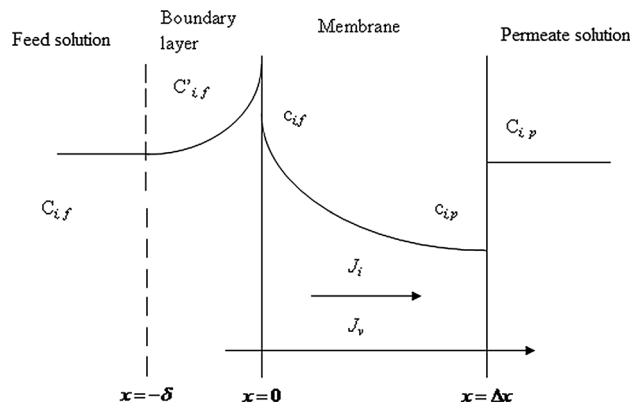


Fig. 1 Solute concentration profiles in the membrane and the feed boundary layer. $C_{i,f}$ is the feed concentration of component i at the membrane surface and $C_{i,p}$ is the permeate concentration on the membrane surface at the permeate side. The permeability depends on the concentration and since there is a concentration profile in the boundary layer, the permeability will be a function of the coordinate x

successful in predicting ion retentions in dilute solutions of single and multiionic solutions (Bowen and Welfoot 2002; Szymczyk and Fievet 2005, 2006; Schlogyl 1966).

Pore model using extended Nernst–Planck equation

The extended Nernst–Planck equation was proposed by Schlogyl (1966), Dresner (1972), and this forms the basis of the description of ion transport through the membranes. This equation covers the three important aspects in transport mechanism, viz diffusion, convection, and electromigration. Explanation of pore model using extended Nernst–Planck equation is based on several assumptions listed below:

- (1) The solution is assumed to be an ideal solution. This enables the effects of coupling between the components in the solution to be neglected.
- (2) All the ions that exist in the membrane are transportable.
- (3) The charge capacity is uniform at any point within the separation zone in the membrane.
- (4) The Donnan equilibrium takes place at the interface between the membrane and the outer solution.

The extended Nernst–Planck equation, which was proposed by Schlogyl, Dresner, and Johnson, is given by:

$$j_i = -c_i D_{i,p} \left(\frac{d}{dx} \mu_i \right) + K_{i,c} c_i J_v \quad (17)$$

Here, j_i is the flux of ion i , $D_{i,p}$ is the bulk permeability of the ion i , μ_i is the electrochemical potential of ion i , and $K_{i,c}$ and $K_{i,d}$ are convective and diffusion hindrance factors,

respectively. The electrochemical potential μ_i can be expressed as:

$$\mu_i = R_g T \ln a_i + V_{si} P + z_i F \psi + \text{constan } t \quad (18)$$

where R_g the gas constant, T is the absolute temperature, V_{si} is the specific volume of ion i , P is the operating pressure, z_i is the valence of ion i , F is the Faraday constant, a_i is the activity coefficient of ion i , and ψ is the electrical potential across the membrane. Substituting Eqs. (18) into (17) yields:

$$j_i = c_i D_{i,p} \frac{d}{dx} \ln a_i - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\psi}{dx} - \frac{c_i D_{i,p}}{RT} V_{si} \frac{dP}{dx} + K_{i,c} c_i J_v \quad (19)$$

The third expression on the left-hand side of Eq. (19) is equal to zero; this is applicable for low-pressure cases (Dickson 1988); hence, the pressure effect is neglected. With $\frac{dP}{dx} = 0$, Eq. (19) is reduced to:

$$j_i = c_i D_{i,p} \frac{d}{dx} \ln a_i - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\psi}{dx} + K_{i,c} c_i J_v \quad (20)$$

The activity coefficient a_i for solute in the capillary is expressed as $a_i = c_i \gamma_i$. By substituting $d \ln a_i = \frac{d a_i}{a_i}$ into Eq. (20) gives:

$$j_i = - \frac{D_{i,p}}{\gamma_i} \frac{d(c_i \gamma_i)}{dx} - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\psi}{dx} + K_{i,c} c_i J_v \quad (21)$$

By simplifying the integration of $\frac{d(c_i \gamma_i)}{dx}$, Eq. (21) yields:

$$j_i = -c_i D_{i,p} \left(\frac{d \ln \gamma_i}{\gamma_i} \right) - D_{i,p} \frac{dc_i}{dx} - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\psi}{dx} + K_{i,c} c_i J_v \quad (22)$$

$\frac{d \ln \gamma_i}{\gamma_i}$ was neglected by Schlogyl (1966), which finally reduces the extended Nernst–Planck equation to:

$$j_i = -D_{i,p} \frac{dc_i}{dx} - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\psi}{dx} + K_{i,c} c_i J_v \quad (23)$$

where $D_{i,p} = K_{i,d} D_{i,\infty}$, j_i is the flux of ion i and the terms on the right-hand side of Eq. (23) represent the transport due to diffusion, electro-migration, and convection, respectively.

A model of electrostatic and steric hindrance model which is a combination of steric hindrance pore and space charge model was developed by Deen et al. (1980), Wang et al. (1995b, 1997) in order to combine both steric and Donnan effects. They apply electrostatic and steric effects to describe the behavior of solute separation through the membrane. The following assumptions were made by Wang et al. (1995a):

- The membrane was assumed to consist of a bunch of capillary with pore radius, r_p , ratio of membrane surface porosity to membrane thickness, $A_K/\Delta x$, and

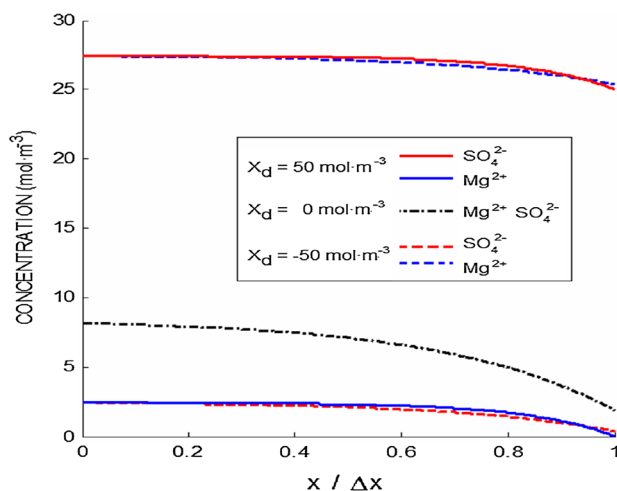


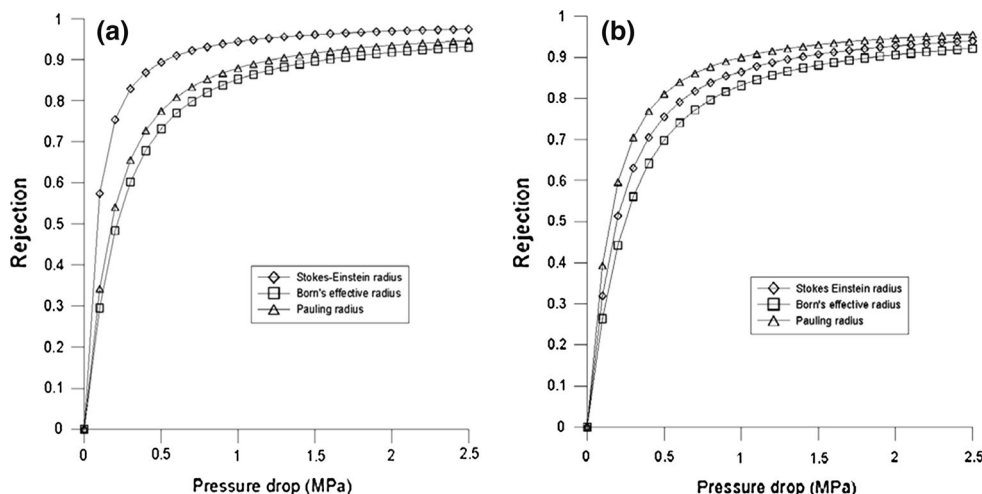
Fig. 2 Ion concentrations along the membrane thickness for three different effective membrane charges (adapted from Gozálviz-Zafrillaa and Santafé-Moros 2008)

surface charge density, q_w , and negatively charged membrane. Where A_K is the ratio of pore cross sectional area over effective cross sectional area of the membrane and Δx is the membrane thickness.

- The steric hindrance effect was only considered for large ion (Stokes radius, r_s was evaluated from Stokes–Einstein).
- The organic electrolyte was distributed completely into large ion and small ion.
- The ion flux and pure water velocity (such as solvent) phenomenon in the membrane capillary was represented by the extended Nernst–Planck equation and Hagen–Poiseuille, respectively (Wang et al. 1995a).
- The ion concentration distribution in the membrane capillary obeys the Poisson–Boltzmann or Donnan equilibrium (Wang et al. 1995a).
- The contribution of organic solutions toward the radial and axial electrical potential distributions is assumed to be negligible for a ternary system, which is water/inorganic electrolyte/organic electrolytes.

Gozálviz-Zafrillaa and Santafé-Moros (2008) used extended Nernst–Planck equation under different physical modes to show the ion concentration profiles obtained at three different membrane charges for the nanofiltration of the magnesium sulfate solution of 50 mol/m^3 . Figure 2 shows ion concentrations along the membrane thickness for three different effective membrane charges. Their investigation shows that a positive membrane charge causes a higher concentration of the anion inside the membrane, being in this case slightly smaller than in the feed because of the steric effect. On the other hand, the positive charge causes a drastic decrease of the cation concentration in the

Fig. 3 **a** Sodium chloride rejection for various radii (Stokes–Einstein, Born’s effective, Pauling) at $\zeta = 0.50$, $r_p = 0.5$ nm. **b** Sodium chloride rejection for various radii (Stokes–Einstein, Born’s effective, Pauling) at $\zeta = -0.50$, $r_p = 0.5$ nm (adapted from Hussain et al. 2007)



membrane. Inversely, for the case of a negative charge, the anion concentration is lower and the cation concentration is higher. All the effects mentioned have a decisive influence on the transport mechanism of ions through the membrane.

Wang et al. (1995a) successfully proved that the rejection of natural solute was only affected by the steric hindrance factor. Other researchers (Hussain et al. 2007) have also studied the effect of various ion sizes on a charged solute rejection, using the Donnan steric pore model and dielectric exclusion model. Dielectric exclusion arises due to the difference in polarization charges, which results in difference in the dielectric constant between the bulk and nanocavity (Hussain et al. 2007). Hussain et al. (2007) studied the effect of dielectric exclusion for the simulation for sodium chloride with the reassessed dielectric constant for the corresponding radii as shown in Fig. 3. They compare positive and negative charged membranes. Higher rejection was predicted for the positive charged membrane with the Stokes–Einstein radius when compared to other radii. When the membrane is negatively charged, Pauling’s radius predicted higher rejection. For both cases, Born’s effective radii predicted lower rejection.

Formulation of Donnan steric pore model and dielectric exclusion

The formulation of Donnan steric pore model and dielectric exclusion that is reviewed here will follows the work done by Hussain et al. (2007). Bowen and Welfoot (2002) developed a one-dimensional Donnan steric pore model with dielectric exclusion for transport of electrolytes through nanofiltration membranes. A schematic diagram of the coordinate system used is shown in Fig. 4.

The following simplifying assumptions are used in the derivation of the model equations (Bowen and Yousef 2003):

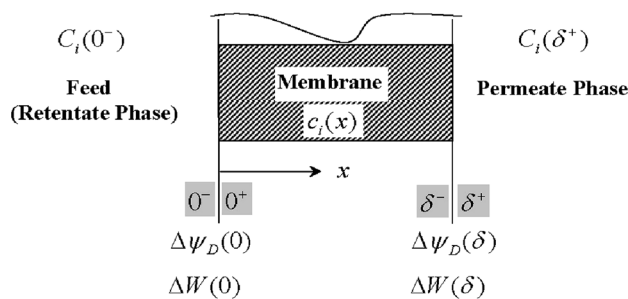


Fig. 4 Coordinate system for the DSPM-DE (adapted from Bowen and Welfoot 2002)

- The solution assumed to behave in an ideal manner.
- Transport inside the pore was due to convection, diffusion, and electro-migration.
- Transport effects with convection and diffusion are corrected with hindrance factors.
- Nanofiltration membrane has porous structure; Hagen–Poiseuille type relationship was used for solvent velocity.
- The flow inside the pore was assumed laminar.
- Chemical potential of solute depends on operating pressure.
- The solvent within the pores consisted of one layer of oriented water molecules.
- Variation of solvent viscosity and dielectric constant inside the pore are considered.
- Concentration polarization across the surface of the membrane was neglected.
- Partial molar volume and diffusion coefficient inside the pore are independent of concentration. The separation at the pore interface was due to steric, Donnan effect, and dielectric exclusion.
- Electroviscous term was neglected for the velocity of the ions in the solvent.

- The concentration and potential gradient were varied axially, and radial variation is neglected. Lateral solute concentration distribution at the pore entrances was ignored.

The molar flux of ion i is given by the extended Nernst–Planck equation as follows:

$$j_i = K_{ic}c_i u + \left(\frac{-c_i D_{ip} d\mu_i}{RT dx} \right) \quad (24)$$

where u is the solvent velocity and K_{ic} is a hindrance factor accounting for the effects of pores walls on the species motion and it is given thus:

$$K_{ic} = (2 - \varphi_i)(1.0 + 0.054\lambda_i - 0.988\lambda_i^2 + 0.441\lambda_i^3) \quad (25)$$

where φ_i is the dimensionless steric partition coefficient of ion i and may be expressed thus:

$$\varphi_i = (1 - \lambda_i)^2 \quad (26)$$

where λ_i is the dimensionless ratio of ion or solute radius i (r_i) to the effective pore radius (r_p) and it is given as follows:

$$\lambda_i = \frac{r_i}{r_p} \quad (27)$$

And D_{ip} is the pore diffusion coefficient of ion i and may be expressed thus:

$$D_{ip} = K_{id} D_{i\infty} \frac{\eta_0}{\eta} \quad (28)$$

where K_{id} is the ionic hindrance factor for diffusion accounting for the effect of pore to reduce the solute–solvent diffusion coefficient below its value in the free bulk solution (water) and $D_{i\infty}$, i.e., the diffusivity of species i in water at infinite dilution; K_{id} may be written as:

$$K_{id} = 1.0 - 2.30\lambda_i + 1.154\lambda_i^2 + 0.224\lambda_i^3 \quad (29)$$

The pore diffusion coefficient, D_{ip} of ion i , is affected by the change of the viscosity, inside the pore η . Many researchers have shown that that the viscosity inside the pore increases by a decrease in pore radius (Bowen and Yousef 2003). The viscosity ratio is given by:

$$\frac{\eta}{\eta_0} = 1.0 + 18 \left(\frac{d}{r_p} \right) - 9 \left(\frac{d}{r_p} \right)^2 \quad (30)$$

where η_0 is the bulk solvent viscosity; while the electrical potential is already been expressed in Eq. (18). Differentiating Eq. (18) and substituting it in Eq. (24) yields:

$$j_i = K_{i,c}c_i(x)u - D_{ip}c_i(x)\partial_x \ln \gamma_i - D_{ip}\partial_x c_i(x) - \frac{1}{RT}V_i D_{ip}c_i(x)\partial_x P - \frac{F}{RT}z_i D_{ip}c_i(x)\partial_x \psi \quad (31)$$

Since the concentration inside the pore is very small, the activity coefficient term in Eq. (31) is neglected according to the Debye–Huckel theory (Bowen and Welfoot 2002). The Hagen–Poiseuille equation for laminar flow is used to give a constant pressure gradient along the pore as follows:

$$\partial_x P = \frac{\Delta P_e}{\Delta x} = \frac{8\eta u}{r_p^2} \quad (32)$$

where ΔP_e is the effective pressure and it is given as:

$$\Delta P_e = \Delta P - \Delta \pi \quad (33)$$

where ΔP and $\Delta \pi$ are the applied and osmotic pressure difference across the pore. Substituting Eqs. (32) into (31) yields:

$$j_i = \left[K_{ic} - \left(\frac{8\eta}{RT r_p^2} \right) D_{ip} V_i \right] c_i u - D_{ip} \frac{dc_i}{dx} - \frac{F}{RT} z_i D_{ip} c_i \frac{d\psi}{dx} \quad (34)$$

Equation (33) consists of three transport terms viz convection, ionic diffusion, and electro-migration. The molar flux j_i is also linked by the filtration condition:

$$j_i = C_i(\delta^+)u \quad (35)$$

Substituting Eqs. (35) into (34), yields:

$$\frac{dc_i}{dx} = \left[\left[K_{ic} - \left(\frac{8\eta}{RT r_p^2} \right) D_{ip} V_i \right] c_i - C_i(\delta^+) \frac{u}{D_{ip}} - \frac{F}{RT} z_i c_i \frac{d\psi}{dx} \right] \quad (36)$$

Multiplication of Eq. (36) by z_i and summation over all the ions give:

$$\sum_{i=1}^n \frac{dc_i}{dx} = \sum_{i=1}^n \left[\left[K_{ic} - \left(\frac{8\eta}{RT r_p^2} \right) D_{ip} V_i \right] c_i - C_i(\delta^+) \frac{z_i u}{D_{ip}} - \frac{F}{RT} \left(\sum_{i=1}^n z_i^2 c_i \right) \frac{d\psi}{dx} \right] \quad (37)$$

The ion concentrations are bounded by electroneutrality conditions as follows:

- For external solution,

$$\sum_{i=1}^n z_i C_i(0^{-1}) = 0, \quad \sum_{i=1}^n z_i C_i(\delta^+) = 0 \quad (38)$$

- For internal solution,

$$\sum_{i=1}^n z_i c_i(x) = \chi_d \quad (39)$$

where χ_d is the membrane volumetric charge density; the

differentiation of Eq. (39) and substituting in Eq. (37) yields:

$$\frac{d\psi}{dx} = \frac{\sum_{i=1}^n \left[\left[K_{ic} - \frac{8\eta}{RT r_p^2} D_{ip} V \right] c_i - C_i(\delta^+) \right] \frac{z_i u}{D_{ip}}}{\frac{F}{RT} \sum_{i=1}^n z_i^2 c_i} \quad (40)$$

The assumption of quasi-equilibrium at the feed and permeate membrane interfaces will allow the ionic concentration within the pore to be related to the feed and permeate concentrations through partition coefficients. The ionic partition coefficient of ion *i* accounts for different physicochemical interactions between the ions in solution and between the ions in the pores and the membrane matrix and may be written as Hussain et al. (2007):

$$k_i = [\text{Steric}] \times [\text{Electrostatic (Donnan)}] \times [\text{Solvation (Born)}] \times [\text{Dielectric}] \quad (41)$$

Equations (36) and (40) form a boundary value problem with the following boundary conditions:

At $x = 0$

$$k_i|_0 = \frac{c_i(x)|_{x=0^+}}{C_i(0^-)} = \varphi \exp\left(-\frac{Fz_i}{RT} \Delta\psi_D(0)\right) \exp\left(-\frac{\Delta W_i(0)}{kT}\right), \quad (42a)$$

$$\sum_{i=1}^n z_i C_i(0^-) \varphi_i \exp\left(-\frac{Fz_i}{RT} \Delta\psi_D(0)\right) \exp\left(-\frac{\Delta W_i(0)}{kT}\right) \quad (42b)$$

At $x = \delta$

$$k_i|\delta = \frac{c_i(x)|_{x=\delta^-}}{C_i(\delta^+)} = \varphi \exp\left(-\frac{Fz_i}{RT} \Delta\psi_D(\delta)\right) \exp\left(-\frac{\Delta W_i(\delta)}{kT}\right) \quad (43a)$$

$$\sum_{i=1}^n z_i C_i(\delta^+) \varphi_i \exp\left(-\frac{Fz_i}{RT} \Delta\psi_D(\delta)\right) \exp\left(-\frac{\Delta W_i(\delta)}{kT}\right) \quad (43b)$$

where the Donnan potential (ψ_D) for the feed and permeate side are, respectively, given by:

$$\Delta\psi_D(0) = \psi(0^+) - \psi(0^-) \quad (44a)$$

$$\Delta\psi_D(\delta) = \psi(\delta^-) - \psi(\delta^+) \quad (44b)$$

where ΔW_i is the solvation energy barrier; with which is estimated from the Born model as follows (Hussain et al. 2007):

$$\Delta W_i = \frac{z_i^2 e^2}{8\pi\epsilon_0 r_i} \left[\frac{1}{\epsilon_p} - \frac{1}{\epsilon_b} \right] \quad (45)$$

where ϵ_p and ϵ_b are dimensionless pore and bulk dielectric constants, respectively. The average pore dielectric

constant ϵ_p can be obtained by assuming that the wall of the pore is covered with one layer of oriented water molecules of thickness (d) and dielectric constant ϵ^* and the inner part of the pore has the bulk dielectric constant ϵ_b . The ϵ_p may be expressed:

$$\epsilon_p = \frac{\int_0^{r_p-d} 2\pi r \epsilon_b dr + \int_{r_p-d}^{r_p} 2\pi r \epsilon^* dr}{\pi r_p^2} = \epsilon_b - 2(\epsilon_b - \epsilon^*) \left(\frac{d}{r_p}\right) + (\epsilon_b - \epsilon^*) \left(\frac{d}{r_p}\right)^2 \quad (46)$$

The pore wise rejection of solute *i* is given by:

$$R_i = 1 - \frac{C_i(\delta^+)}{C_i(0^-)} \quad (47)$$

For uncharged solute, $\frac{d\psi}{dx} = 0$, Eq. (36) thus reduces to:

$$\frac{dc_i}{dx} = \left[\left[K_{ic} - \left(\frac{8\eta}{RT r_p^2}\right) D_{ip} V_i \right] c_i - C_i(\delta^+) \frac{u}{D_{ip}} \right] \quad (48)$$

Using the following boundary conditions:

At $x = 0$

$$k_i|_0 = \frac{c_i(x)|_{x=0^+}}{C_i(0^-)} = \varphi_i \quad (49a)$$

At $x = \delta$

$$k_i|\delta = \frac{c_i(x)|_{x=\delta^-}}{C_i(\delta^+)} = \varphi_i \quad (49b)$$

Equation (48) can be integrated (with the boundary conditions) to give an analytical relationship for the uncharged solute rejection as follows:

$$R_i = 1 - \frac{(K_{ic} - \beta_i) \varphi_i}{1 - [1 - (K_{ic} - \beta_i)] \exp(P_{ei})} \quad (50)$$

where β_i and P_{ei} are the dimensionless quantity and dimensionless modified Peclet number.

where $\beta_i = \frac{8\eta}{RT r_p^2} D_{ip} V_i$, $P_{ei} = \frac{(K_{ic} - \beta_i) r_p^2 \Delta P_c}{8\eta D_{ip}}$.

Donnan steric pore model has been identified as the most appropriate and accurate predictive model for the characterization of nanofiltration membranes separation process since this model was developed based on the extended Nernst–Planck equation that consider all of the transport mechanisms i.e., diffusion, electro-migration, and convection.

Conclusion

Nanofiltration is widely used in the industry; properties achieved from the data that are obtained from theoretical characterization of the nanofiltration membranes allow for

novel separations that are difficult or expensive to achieve with other separation methods. The characterization of nanofiltration membranes for wastewater treatment is becoming more important for membrane users, membrane manufacturers, and membrane technologies. The best characterization is needed for the selection of an appropriate membrane for specific application in order to understand and predict separation performance for various substances. Therefore, useful predictive models are very important in process performance prediction, process design, and optimization. In a theoretical model development, the model derivation is basically based on the irreversible thermodynamic approach and the hydrodynamic approach. These approaches have been used by various researchers in order to determine the ion transport mechanisms during separation process. These transport mechanisms are commonly governed by steric and charge effects. The charge of nanofiltration membranes is usually determined by streaming line potential, but a good theoretical model can be used to predict the rejection of ions obtained from experiments. Researchers have found that the extended Nernst–Planck equation or hydrodynamic approach is more interesting and applicable in industries due to its description which illustrates the ionic transport mechanisms in more comprehensive and detailed manner. This approach includes the three ion transport mechanisms in membrane separation, viz diffusion, electromigration, and convection.

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