Review of Basics Reverse Osmosis Process Modeling: A new combined fouling index proposed

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Abstract

Seawater desalination is currently considered to be one of the primary technologies to resolve the global water scarcity problem. A basic understanding of membrane filtration phenomena is significant not only for further technological development but also for integrated design, optimal control, and long-term maintenance. In this vein, the present work reviews the major transport and filtration models, specifically related to reverse osmosis phenomena, provides theoretical insights based on statistical mechanics, and discusses model-based physical meanings as related to their practical implications.

Keywords: Reverse Osmosis; Concentration Polarization; Solution-diffusion model; combined fouling index (CFI); Modified Fouling Index (MF); Membrane Process Modeling

1. Introduction

The first commercial reverse osmosis (RO) membrane was developed by two researchers, Loeb and Sourirajan in early 1960 in the Department of Engineering, University of California, Los Angeles (UCLA). After the pioneering work, RO technology has been rapidly developed and widely applied in a variety of separation and filtration fields, especially for seawater desalination. Fig. 1(a) shows original photo images of the prototype desalination cell using fabricated cellulose acetate membranes [1]. Their project entitled “Sea Water Demineralization by Means of Semipermeable Membrane” was carried out under the sponsorship of the Statewide Water Resources Center program in Sea Water Conservation Research. S. Loeb and S. Sourirajan were listed as project leaders, and the other four personnel include Lloyd Graham, A. Noeggerath, R. Sayano, and M. Accomazzo. The report was signed by Prof. J. M. English, vice-chairman of research, in the Department of Engineering, UCLA. Fig. 1(b) shows the “life test assembly” which contains the desalination cell and circulating and pressurizing pumps. The life test indicates the filtration experiment, which operated 24 hours per day for two months. The feed solution was 5.25 percent of seawater (generated within the system), and the applied pressure was 1500 psi (=103.4 bar). During the
first seven days (period 1) from the fall of 1959, water flux and permeate concentration were measured as 6.4 gal/ft² day (≈10.87 liter/m² h, LMH) and 0.042 percent. From the second to the fourth week (period 2), water flux decreased from 5.6 to 5.2 6.4 gal/ft² day and the permeate concentration remained as 0.040± 0.003 percent. In period 1 and 2, the rejection ratios were calculated as 99.20 and 99.24 percent, respectively. In period 3 of four weeks, the average flux was 4.75 gal/ft² day with 98.97 percent of rejection. Finally, the total cost was estimated as $0.60 per 1,000 gallons, i.e., $0.16/m³, which is cheaper than the present water production rate by Sorek plant, in Israel, currently producing 624,000 m³/day (26,000 m³/hour) [2]. In the 1960 report, Loeb and Sourirajan’s future work includes standardization of film-fabricating techniques, fabrication cost estimation, and investigation of separation mechanisms, which have been vigorously conducted by subsequent researchers till date. The fabricated membrane is later explicitly called Loeb-Sourirajan membrane, and the more detailed story can be found elsewhere [3, 4].

Various mechanisms and models were suggested to explain the RO phenomena. The sieving mechanism [5] indicates that the separation occurs because of the difference between molecular sizes of solvent and solutes. The wetted-surface mechanism [6, 7] treats the membrane as very wettable material so that water tends to cling to the membrane surface. The solution-diffusion model [8, 6] followed by the solution-diffusion-imperfection model [10] assumes that both solvent and solutes dissolve in the homogeneous nonporous surface layer of the membrane and then diffuse without significant solvent-solute interactions. The preferential sorption & capillary flow mechanism [5, 11, 12] proposes a critical pore size, twice (or smaller than) the water layer thickness on the membrane surface, to allow only solvent transport through the membrane. Among these models for RO processes, the solution-diffusion model was most widely accepted for explanation and prediction. Transport of solvent and solutes was universally explained using the transmembrane chemical potential and transition from the solution-diffusion to the pore flow was investigated [13]. Later, the solution-diffusion model was reformulated as a pressure-driven diffusion process using rigorous thermodynamic boundary conditions, which led to nonlinear responses at high pressure and the coupling between solvent and solutes was considered using the Maxwell-Stefan formulation for multi-component diffusion [14].

Although the models as mentioned earlier were used to fundamentally explain the RO phenomena, they mostly dealt with specific mass transport mechanisms across the polymer membrane, of which thermodynamic state is assumed to be quite close to the pure static equilibrium. To the best of my knowledge, non-equilibrium thermodynamics is still at a nascent stage in theoretical statistical physics. The front-end improvement is a theory to investigate the thermoelectric phenomena, such as transference phenomena in electrolytes and heat conduction in an anisotropic medium, viewed as coupled, irreversible phenomena [15, 16]. A thermodynamic system was relaxed from the pure equilibrium to one where the microscopic reversibility could be assumed. This means that an irreversible system of non-equilibrium can be viewed
as a collection of a number of small local subregions, having individual processes, in which the time-reversal is guaranteed. The time-reversal indicates that an evolving system from its initial condition returns to the initial state if time $t$ is reversed to $-t$. In other words, an average rate of an individual process is equal to the average rate of its reverse process. In his work, Onsager described the irreversible process using the entropy change rate. A phenomenological driving force was defined as a partial derivative of the entropy with respect to specific fluxes (of multi-species or heat).

The first irreversible transport (IRT) model was developed to explain the transfer of non-electrolytes through membranes by applying Onsager’s reciprocal theorem to the membrane separations by Kedem and Katchalsky [17], followed by Spiegler and Kedem [18]. These irreversible transport models require empirically determining a few model parameters, which is a practical trade-off to use more realistic models. Most membrane systems are thermodynamically open to the ambient environment. If one of the systems is in a thermodynamic state that is quite close to a static equilibrium, then the irreversible model parameters often converge to those of limiting values of the pure equilibrium. In this case, irreversible thermodynamic filtration models become mathematically identical to the solution-diffusion model regarding functional interdependences between the solvent and solute fluxes and their relationship with the effective driving force.

More rigorous theoretical investigation of RO processes using the non-equilibrium thermodynamics or simply steady-state thermodynamics is necessary to develop next-generation membrane technology. Currently, there are a number of excellent articles that provide well summarized technical information and future perspectives of RO technology [19-27]. Continuing in this vein, the current work will deal with in-depth and detailed analysis of the solution-diffusion model in various aspects as applied to process simulations with a limited literature review and provide theoretical derivations for the fouling phenomena on the RO membrane. Fundamental studies and reviews on the future membrane technologies in various aspects can be found elsewhere [28-32]. This paper aims to provide a clear picture of the RO membrane as a platform of coupled thermo- and fluid dynamic phenomena and contribute to a solid curriculum for membrane engineering.

### 2. Theory and Simulation Review

#### 2.1. Basic RO process modeling

##### 2.1.1. Mass balance equations

Fig. 2 shows the RO schematic, consisting of ten thermodynamic and fluid dynamic variables. Hydraulic pressure $\Delta P$ is applied to the feed stream of concentration $C_f$ and results in feed flow rate $Q_f$. A portion of the feed stream passes through the RO membrane characterized by solvent permeability $A$, solute permeability $B$, and surface area $A_m$. This product stream is called permeate stream having concentration $C_p$ (usually much lower than $C_f$) and outflow rate $Q_p$. The concentrate (often
called retentate) stream has concentration \(C_c\) (higher than \(C_f\) due to the solvent permeation) flowing with its outflow rate \(Q_c\). The study objective of this basic RO modeling is to calculate output concentrations and flow rates in terms of input and operating conditions. Here we define two representative parameters used to evaluate the performance of RO membranes: rejection ratio (which we will later call observed rejection)

\[
R = 1 - \frac{C_p}{C_f}
\]  

(1)

and recovery ratio

\[
Y = \frac{Q_p}{Q_f}
\]  

(2)

which express the quality and quantity of the solvent product, respectively.

For both solvent and solute mass transport, the input rate is equal to a sum of two output rates:

\[
Q_f = Q_p + Q_c
\]  

(3)

\[
C_fQ_f = C_pQ_p + C_cQ_c
\]  

(4)

Solvent flux \([\text{m/sec}]\), i.e., the collected volume of water transported through the membrane per unit time per unit membrane surface area, is described as

\[
J_w = \frac{Q_p}{A_m} = A_m(\Delta P - \Delta \pi)
\]  

(5)

where \(\Delta \pi = \pi_f - \pi_p\) is the osmotic pressure difference between the feed (\(\pi_f\)) and the permeate (\(\pi_p\)) streams. Solute flux, i.e., the solvent flux multiplied by permeate concentration \([\text{mg/l} \cdot \text{m/sec}]\) is expressed as

\[
J_s = B (C_f - C_p)
\]  

(6)

\[
= C_pJ_w
\]  

(7)

Substituting Eq. (2) in (4) allows us to express the retentate concentration using feed and permeate concentrations and recovery ratio:

\[
C_c = \frac{C_f - C_pY}{1 - Y}
\]  

(8)

The permeate concentration of Eq. (7) is rewritten as

\[
C_p = \frac{J_s}{J_w} = \frac{C_f}{1 + \frac{B}{C_p}(\Delta P - \Delta \pi)}
\]  

(9)

and flow rates of the permeate and retentate streams are then represented using \(Q_f\) and \(Y\):

\[
Q_p = Q_fY
\]  

(10)

\[
Q_c = Q_f(1 - Y)
\]  

(11)
Note that we initially had total ten variables (shown in Fig. 2), of which subset consists of six knowns: \{\Delta P, A, B, A_\alpha, C_f, Q_f\}. The four balance equations (3)-(8) of solvent and solute transfer rates make the RO process modeling mathematically solvable.

2.1.2. Analytic solutions with van’t Hoff-type osmotic pressure

If the osmotic pressure is linearly proportional to the solute concentration, then its transmembrane difference is

\[ \Delta \pi = b \left( C_f - C_p \right) \]  

where \( b \) is a proportionality. In van’t Hoff’s equation, we have \( b = RT \), where \( R \) is the gas constant and \( T \) is the absolute temperature of the membrane system. (J. H. van’t Hoff was recognized by the Nobel Prize committee for his discovery of “the laws of chemical dynamics and osmotic pressure in solutions” and received the first Nobel Prize in Chemistry in 1901.) Substitution of (12) into (9) gives

\[ C_p = C_\alpha \left[ \sqrt{1 + C_\beta^2/C_\alpha^2} - 1 \right] \]  

where

\[ C_\alpha = \frac{BA^{-1} + \Delta P - bC_f}{2b} \] \hspace{1cm} (14)

and

\[ C_\beta = \sqrt{\frac{BC_f}{Ab}} \] \hspace{1cm} (15)

Note that \( C_\alpha \) and \( C_\beta \) have a unit of solute concentration. For simplicity, let’s set  \( \psi = C_\beta/C_\alpha \). If \( \psi \ll 1 \), then one can approximate the terms in the parenthesis of Eq. (13) using the Taylor expansion as

\[ \sqrt{1 + \psi^2} - 1 = \left[ 1 + \frac{1}{2} \psi^2 + \cdots + O(\psi^4) \right] - 1 \approx \frac{1}{2} \psi^2 = \frac{1}{2} \left( \frac{C_\beta}{C_\alpha} \right)^2 \] \hspace{1cm} (16)

where \( O(\psi^4) \) indicates the remaining terms of \( \psi^4 \) and higher, and simplify the functional form of \( C_p \) as

\[ C_p \approx \frac{C_\beta^2}{2C_\alpha} = \frac{C_f}{1 + \frac{A}{B} (\Delta P - \pi_f)} \] \hspace{1cm} (17)

which is equivalent to Eq. (9) with a condition of \( C_p \ll C_f \), and hence indicating \( \Delta \pi \approx \pi_f \). However, note that Eq. (9) is only an implicit solution for \( C_p \), because \( \Delta \pi \) includes \( C_p \) itself. For an accurate calculation, \( C_p \) of Eq. (17) needs to be used to calculate \( \Delta \pi \) in Eq. (12). An iterative method should continue until \( C_p \) in Eq. (9) converges to a specific constant value. The accurate calculation of \( C_p \) is important not only for RO but also for NF, in which \( C_p \) is comparable with \( C_f \). In this case, higher-order terms in Eq. (16) must be important for such low-rejection filtration processes,
in which the straightforward approximation of \( C_p \ll C_f \) in RO is questionable. As the exact solution of Eq. (13) has a perfect closure form, calculations of \( C_c, Q_p \) (or \( J_w \)), and \( Q_c \) are straightforward using \( C_p \) of Eq. (13) without any approximation or numerical iterations.

2.1.3. Causes and effects

Fig. 3 shows how output variables \( C_p, Q_p \) and \( C_c \) change with respect to input variables of \( \Delta P, Q_f \) and \( C_f \), while \( A, B \) and \( A_m \) are assumed to be invariant during operations. Calculation of \( Q_c \) is straightforward using the solvent mass balance. While one of the three input variables changes with the other two remaining fixed, variations of output variables with respect to the solely changing input variable are analyzed as follows using Eqs. (8)–(10). Fundamental aspects of the solution-diffusion model will be discussed in the later sections.

Effect of pressure \( \Delta P \). First, we let \( C_f \) and \( Q_f \) remain constant and increase only applied pressure \( \Delta P \). This type of analysis is mathematically equivalent to calculating partial derivatives of \( C_p, Q_p \) and \( C_c \) with respect to \( \Delta P \).

(a) In most RO cases of a high rejection ratio close to 1.0, \( B \ll J_w \) must be a good approximation in RO processes. (Note that \( B \) and \( J_w \) have the same unit of velocity [m/s].) As \( J_w \) is proportional to \( \Delta P \), the permeate concentration \( C_p \) of Eq. (9) decreases with \( \Delta P \):

\[
\frac{C_p}{C_f} = \frac{1}{1 + J_w/B} \approx \frac{B/A}{(\Delta P - \Delta \pi)}
\]  

(18)

If concentration polarization is negligible above the membrane surface, one can approximate \( \Delta \pi \approx \pi_f \). \( C_p \ll C_f \), and hence \( C_p \propto 1/\Delta P \). One may apply a higher pressure to decrease the permeate concentration \( C_p \) to be obtained by increasing water flux \( J_w \) through the membrane. If the feed concentration is close to the seawater concentration having the osmotic pressure about 400 – 500 psi, then a decrease in \( C_p \) with respect to \( \Delta P \) is not as much as that of brackish water of a few thousand mg/l. As one increases \( \Delta P \), the enhanced pressure pushes more water to the membrane to have a higher permeate flux, \( J_w \). In this case, the convective solute transport (roughly equal to \( C_f J_w \)) increases at the membrane surface. As the membrane rejects solute ions, \( C_m \) increases from \( C_f \), providing a higher osmotic pressure difference between the feed side and the permeate side of membrane surface, i.e., \( \Delta \pi_m = \pi_m - \pi_p > \Delta \pi_f = \pi_f - \pi_p \). The increase in \( \Delta \pi_m \) is a partial feedback from increased \( \Delta P \), so that a decrease in \( C_p \) is lessened by the \( C_p \) phenomena, which is fundamentally inevitable.

(b) The permeate flow rate is conceptually equivalent to the permeate flux, because the available membrane surface area \( A_m \) is usually fixed. (See Eq. (3).) This indicates that the variation of \( Q_p \) with respect to \( \Delta P \) is the same as that of \( J_w \). Here, we assume for simplicity that \( \Delta \pi \) is insensitive to \( \Delta P \), and \( J_w \) is not
meaningful for $\Delta P \leq \Delta \pi$. As indicated in Fig. 3(b), the onset of non-zero $Q_p$ occurs when $\Delta P$ exceeds $\Delta \pi$. After that, $Q_p$ monotonously increases with $\Delta P$ and the slope is equal to $A \cdot A_m$ from Eq. (5). In reality, measured $Q_p$ resides below the linear line, because the $C_p$ increases the osmotic pressure difference and therefore decreases the effective pressure, $\Delta P_{\text{eff}} = \Delta P - \Delta \pi_m$.

(c) As $C_p$ decreases with respect to $\Delta P$, more solutes are rejected by the membrane. Overall, the amount of solutes retained per unit volume, i.e., retentate concentration $C_c$, increases with $\Delta P$. For high rejection of $C_p \ll C_f$, we can neglect $C_pY = C_f(1 - R)Y$ in the numerator of Eq. (8):

$$C_c \approx \frac{C_f}{1 - Y}$$  \hspace{1cm} (19)

Note that $Y$ is proportional to $Q_p \propto J_w \propto \Delta P_{\text{eff}}$. $C_c$ is therefore linearly proportional to $\Delta P$ if and only if the recovery ratio is small (i.e., $Y \ll 1$). To validate this, one can use Taylor’s series of $C_c$ with respect to $Y$:

$$C_c \approx C_f \left(1 + Y + O(Y^2)\right)$$  \hspace{1cm} (20)

Otherwise, the higher-order terms become significant and $C_c$ must non-linearly increase with $\Delta P$.

**Effect of feed flow rate $Q_f$.**

(d) The feed flow rate $Q_f$ usually does not significantly change the characteristics of the permeate stream, unless $\Delta P$ depends on $Q_f$. The permeate concentration is pseudo-independent of $Q_f$.

(e) In the same vein, the permeate flow rate is indifferent to the feed flow rate because $Q_p$ primarily depends on the applied pressure $\Delta P$. The amount of water that passes in the longitudinal direction (tangentially to the membrane surface) in the feed stream does not noticeably change the permeate flux $J_w$ or permeate flow rate $Q_p$.

(f) Because $Q_f = Q_p + Q_c$, for a constant $Q_p$, $Q_c$ increases with $Q_f$. Eq. (19) can be then rewritten as

$$C_c = C_f \frac{Q_f}{Q_c} = C_f \left(1 + \frac{Q_p}{Q_f - Q_p}\right)$$  \hspace{1cm} (21)

to show $C_c$ gradually decreases with $Q_c$ or $Q_f$.

**Effect of feed concentration $C_f$.**

(g) When the applied pressure is much higher than the feed osmotic pressure, $C_p$ is linearly proportional to $C_f$; in other words, $C_p/C_f = \text{constant}$. When the feed applied pressure is comparable with the osmotic pressure, $C_p$ versus $C_f$ curve shows a non-linearly increasing trend, which is above the linear line. Eq. (5)
indicates that the increase in $C_f$ secondarily contributes to $\Delta \pi_m$, increases $C_m$, and finally reduces $\Delta P_{ef}$ and $J_w$. As a consequence, the solvent and solute fluxes decrease and increase, respectively, with respect to $C_f$, and therefore the permeate concentration increases.

(h) When $\Delta P$ and $Q_f$ are fixed, $Q_p$ linearly decreases with respect to the feed concentration:

$$Q_p = A_m J_w \propto \Delta P - \Delta \pi_m = \Delta P + bC_p - bC_m$$

The permeate flow rate vanishes when $\pi_m = \Delta P + \pi_{sp} \approx \Delta P$.

(i) When recovery is small, i.e., $Y \ll 1$ or $Q_p \ll Q_f$, the retentate concentration $C_c$ does not change significantly from the feed concentration level, i.e., $C_c \approx C_f$. As $C_f$ increases when $\Delta P$ is finitely higher than $\pi_{sp}$, $Y$ decreases because $Q_p$ monotonously decreases with $C_f$. Therefore, the slope of $C_c$ versus $C_f$ plotted from Eq. (8) also decrease with $C_f$: $1/(1 - Y) \approx 1 + Y + Y^2 + Y^3 + \cdots$. Note that $(1 - Y)^{-1} > 1$ indicates $C_c$ is unconditionally higher than $C_f$, except for the zero-recovery case. The slope of Fig. 3 can be calculated as

$$\frac{\partial C_c}{\partial C_f} = \frac{1 - Y_0}{[1 - Y_0 + Y_1 C_f]^2}$$

where $Y_0 = A_m A \Delta P/Q_f$ and $Y_1 = A_m Ab/Q_f$. Using parameter values in Fig. 3 gives the $Y_0$ value higher than 1.0, which provides a negative value of $\partial C_c/\partial C_f$, and therefore Fig. 3(i) shows the gradually decreasing behavior of $C_c$ with respect to $C_f$.

2.2. Concentration Polarization

2.2.1. Phenomena

Fig. 4 shows a schematic of diffusive and convective transport of solutes near the membrane surface. During the RO/NF filtration process, pressurized feed stream of concentration $C_f$ flows in a tangential ($x$-) direction to the membrane with velocity $u$. Solutes are rejected by the membrane, whereas solvent (water) molecules pass through the membrane. The permeate concentration $C_p$ is therefore much lower than the feed concentration $C_f$ in proper operations. The hydraulic pressure gradient between the bulk and permeate stream generates the solvent flow across the membrane, which is defined as the permeate flux $J_w$ i.e., the volume of solvent passing through the membrane per unit membrane surface area: a unit of $J_w$ is [m$^3$/m$^2$ s], equivalent to [m/s] or [µm/s]. As the transverse solvent flow brings solutes down to the membrane surface, solutes are retained on the membrane surface where concentration $C_m$ is higher than $C_f$. This phenomenon of the uneven or biased concentration distribution near the membrane surface is called the concentration polarization (CP), and the region where the CP occurs is called the CP layer. $\delta_p$ denotes the thickness of the CP layer above which the concentration remains $C_f$. 
2.2.2. Mass balance

Solutes are transported from the bulk phase toward the membrane by two mass transfer mechanisms, i.e., convection and diffusion, which are balanced as

\[ J_w C - (-D \frac{\partial C}{\partial y}) = J_w C_p \]  

(24)

Here, \( J_w C \) is the convective transport of solutes from the bulk phase toward the membrane. Within the concentration polarization layer, \( 0 < y < \delta_p \), the solute concentration \( C(y) \) decreases with respect to \( y \) so that \(-D \frac{\partial C}{\partial y}\) is positive and indicates the magnitude of diffusive transport of solutes from the membrane surface to the bulk phase. Therefore, specific boundary conditions are:

\[ C(y = 0) = C_m \]  

(25)

\[ C(y = \delta_p) = C_f \]  

(26)

The CP layer of thickness \( \delta_p \) is usually much smaller than the channel height of the feed flow. Within the CP layer, it is appropriate to approximate that the permeate flux \( J_w \) is constant with respect to \( y \) and the concentration is independent of the axial position \( x \) of the membrane surface. Then, the partial derivative of \( \partial C/\partial y \) in Eq. (24) becomes its ordinary differential, i.e., \( dC/dy \). Integration of Eq. (24) with respect to \( y \) using boundary conditions of Eqs. (25) and (26) yields

\[ \frac{C_m - C_p}{C_f - C_p} = e^{J_w/k_f} \]  

(27)

where \( k_f = D/\delta_p \) is the mass transfer coefficient, indicating how quickly solutes back-diffuse from the membrane to the bulk phase. (See Appendix A.1 for the detailed derivation of Eq. (27)). Usually, \( \delta_p \) (or \( k_f \)) is unknown and often estimated using empirical correlations, because a coupled mass transfer equation using varying cross-flow velocity is hard to solve. The right-hand side of Eq. (27) is interpreted as the ratio of excessive concentrations at the membrane surface to that of the bulk phase. In RO/NF, this ratio is about 2–3.

2.2.3. Rejection ratios

From Eq. (27), the solute concentration on the membrane surface is rewritten as

\[ C_m = C_p + (C_f - C_p) e^{J_w/k_f} \]  

(28)

\[ C_m = C_p + C_f R_{obs} e^{J_w/k_f} \]  

(29)

where \( R_{obs} \) is the observed rejection ratio, defined as

\[ R_{obs} = 1 - \frac{C_p}{C_f} \]  

(30)
which indicates the fraction of solutes retained by the membrane. The permeate concentration can be calculated using $R_{\text{obs}}$:

$$C_p = C_f (1 - R_{\text{obs}})$$  \hfill (31)

and now we can eliminate $C_p$ in Eq. (29) to derive

$$\frac{C_m}{C_f} = 1 + R_{\text{obs}} \left( e^{J_{w}/k_f} - 1 \right)$$  \hfill (32)

For the perfect rejection ($R_{\text{obs}} = 1$), $C_m$ reduces to

$$C_m = C_f e^{J_{w}/k_f}$$  \hfill (33)

as a product of $C_f$ and the exponential factor. In addition to $R_{\text{obs}}$, the intrinsic rejection is defined as

$$R_{\text{int}} = 1 - \frac{C_p}{C_m} (> R_{\text{obs}})$$  \hfill (34)

Substitution of Eq. (28) in (34) derives

$$\frac{C_m}{C_f} = \frac{e^{J_{w}/k_f}}{R_{\text{int}} + (1 - R_{\text{int}}) e^{J_{w}/k_f}} > 1.0$$  \hfill (35)

which requires known values of $J_w$, $k_f$, and $R_{\text{int}}$. In normal RO processes, measured $J_w$ is about a few $\mu$m/s, $k_f$ can be estimated using empirical correlations, and $R_{\text{int}}$ is often close to 1.0. If the intrinsic rejection $R_{\text{int}}$ is close to zero, the right-hand side converges to one. No concentration polarization occurs and the concentration has an even distribution along the $y$-direction, i.e., $C_m \approx C_f$. Similarly, if the membrane resistance is too high (e.g., almost impermeable when deleteriously fouled), the solvent flux becomes very small, i.e., $J_w \to 0$. Hence, we calculate that:

$$e^{J_{w}/k_f} \approx 1 + O \left( \frac{J_{w}}{k_f} \right) \approx 1.0$$  \hfill (36)

or equivalently $C_m \approx C_f$.

2.3. Solution-diffusion model

2.3.1. Governing equations based on Fick’s law

Solvent Transport. We assume that water transport through the normal membranes is by diffusion through a single phase and write transport equation of water:

$$J_w = -D_w \nabla C_w$$  \hfill (37)

where $C_w$ and $D_w$ are concentration and diffusivity of water dissolved in the membrane. We accept the Henrian approximation that in an isothermal environment

$$\mu_w = RT \ln C_w + \mu_{wo}$$  \hfill (38)
where $\mu_w$ is the chemical potential of the water and $\mu_{wo}$ is an isothermal constant independent of $C_w$. Substitution of Eq. (38) in (37) gives

$$J_w = \frac{D_w C_w}{RT} \nabla \mu_w \approx \frac{D_w C_w}{RT} \frac{\Delta \mu_w}{\delta_m}$$

(39)

which represents the solvent flux driven by the chemical potential gradient $\nabla \mu_w \approx \Delta \mu_w / \delta_m$, where $\Delta \mu_w$ is the chemical potential difference across the membrane of thickness $\delta_m$. In pressure-driven membrane separation processes, the chemical potential of water may be governed by the applied pressure and water concentration and can be expanded as

$$d \mu_w = \left( \frac{\partial \mu_w}{\partial C_w} \right)_{P,T} d C_w + \left( \frac{\partial \mu_w}{\partial P} \right)_{C_w,T} d P$$

(40)

Integration of Eq. (40) across the membrane gives

$$\Delta \mu_w = \int \left( \frac{\partial \mu_w}{\partial C_w} \right)_{P,T} d C_w + \int \left( \frac{\partial \mu_w}{\partial P} \right)_{C_w,T} d P$$

$$= \int \left( \frac{\partial \mu_w}{\partial C_w} \right)_{P,T} d C_w + \bar{v}_w \Delta P$$

(41)

If the applied pressure is equal to the osmotic pressure difference ($\Delta P = \Delta \pi$), then mass fluxes are zero since the chemical potential has zero gradient. Hence, we obtain

$$\int \left( \frac{\partial \mu_w}{\partial C_w} \right)_{P,T} d C_w = -\bar{v}_w \Delta \pi$$

(42)

and therefore

$$\Delta \mu_w = \bar{v}_w (\Delta P - \Delta \pi)$$

(43)

where $\bar{V}_w$ is the molar volume of the solvent. Substitution of Eq. (43) in (39) gives the solvent flux

$$J_w = \frac{D_w C_w \bar{v}_w}{RT \delta_m} (\Delta P - \Delta \pi) = A (\Delta P - \Delta \pi)$$

(44)

where

$$A = \frac{D_w C_w \bar{v}_w}{RT \delta_m}$$

(45)

is called the solvent permeability having a unit of $[m/s\cdot atm]$, which is often assumed to be independent of $\Delta P$. Eq. (44) indicates that the water flux through the membrane is proportional to the effective pressure, i.e. the $\Delta P$ and $\Delta \pi$. The origin of this conclusion is from the thermodynamic relationship:

$$\left( \frac{\partial \mu_w}{\partial P} \right)_{C_w,T} = \bar{v}_w$$

(46)
or equivalently

$$\mu_w = \bar{v}_w \Delta P + f(C_w, T)$$  \hspace{1cm} (47)$$

where $f$ is an arbitrary function of $C_w$ and $T$. Comparison of Eqs. (47) and (40) gives a self-consistent result in terms of specific dependence of $\mu_w$ on $\Delta P$, $C_w$, and $T$.

**Solute Transport.** The transmembrane solute diffusion is also assumed to be Fickian:

$$J_s = -D_s \nabla C_s \approx \frac{D_s}{\delta_m} \Delta C_s = B \Delta C_s$$  \hspace{1cm} (48)$$

where $J_s$, $D_s$, and $C_s$ are the mass flux, diffusivity, and concentration of the solute, respectively, in the membrane. The phenomenological solute transport coefficient can be defined as

$$B = \frac{D_s}{\delta_m}$$  \hspace{1cm} (49)$$

which is called the solute permeability. It is often assumed that $D_s$ is independent of the solute concentration, but may vary with temperature. In Eq. (48), $\Delta C_s$ indicates the transmembrane concentration difference, measured on the exterior surfaces of the membrane.

### 2.3.2. Solvent and solute fluxes

The solvent flux $J_w$ is proportional to the effective pressure, of which the osmotic pressure difference can be more accurately represented as:

$$\Delta \pi = \pi_m - \pi_p$$  \hspace{1cm} (50)$$

The van’t Hoff equation indicates that the (absolute) osmotic pressure is linearly proportional to the solute concentration, unless the concentration is too high near the solubility limit. In this case, the solution-diffusion model is equivalent to the osmotic pressure model and then we have:

$$\Delta \pi = \pi_f \left( \frac{C_m}{C_f} - \frac{C_p}{C_f} \right)$$  \hspace{1cm} (51)$$

and hence using Eq. (32) we make a relationship between the thermodynamic variable $\Delta \pi$ and the hydrodynamic variable $J_w$ through the mass transfer coefficient $k$.

$$\Delta \pi = \pi_f R_{obs} e^{J_w/k_f}$$  \hspace{1cm} (52)$$

By substituting Eq. (52) in (44) we obtain

$$J_w = A \left( \Delta P - \pi_f R_{obs} e^{J_w/k_f} \right)$$  \hspace{1cm} (53)$$

which needs to be solved iteratively for $J_w$ with an estimated value of $k_f$. Phenomenologically, the permeate flux increases if the applied pressure increases. The enhanced
permeate flux contributes additionally to the convective solute transport toward the membrane surface, which brings more solutes on the membrane surface and hence increases $C_m$. The osmotic pressure on the membrane surface $\pi_m$ therefore increases exponentially with $J_w$ (See Eq. 52). As a consequence, the net pressure, the driving force of the solute permeation, does not increase as much as $\Delta P$ increases, because the concentration polarization causes the reduction of the driving force as indicated in Eq. 52. Since $J_w$ is on both sides of Eq. (53), a nonlinear or iterative solver is required to calculate $J_w$. If the mass transfer coefficient is larger than the permeate flux or

$$\frac{J_w}{k_f} < 1 \quad \text{and} \quad \left( \frac{J_w}{k_f} \right)^2 \ll 1,$$

then we can expand the exponential form in Eq. 52 as

$$e^{J_w/k_f} \simeq 1 + \frac{J_w}{k_f} + O \left( \frac{J_w^2}{k_f^2} \right).$$

In this case, we derive an analytic expression for the permeate flux:

$$J_w = A_{eff} (\Delta P - \pi_f R_{obs})$$

under the influence of the $C_p$, where the effective solvent permeability $A_{eff}$ is calculated as

$$A_{eff} = \frac{A}{1 + \pi_f R_{obs} k_f^{-1}} (< 1)$$

Eq. (55) explains the solvent permeation giving a different picture from that of Eq. (53). $\pi_f R_{obs}$ indicates the osmotic pressure difference between the feed and permeate streams. The effective solvent permeability $A_{eff}$, which is smaller than $A$, includes the resistance for solvent permeation from the membrane and the CP layer. When the concentration polarization is negligible and so its thickness is very small, i.e., $\delta_p \to 0$, then the mass transfer coefficient $k_f$ diverges, because a finite concentration difference exists within a CP layer of zero thickness $k_f^{-1} \to 0$. The effective solvent permeability $A_{eff}$ converges to $A$ as the CP layer disappears.

In the solution-diffusion model, the driving force for the solute flux is the concentration difference between the membrane surface and the permeate stream. Replacing $\Delta C_s$ in Eq. 48 by $C_m - C_p$ gives

$$J_s = B \left( C_m - C_p \right)$$

where $B$ has the same unit of $J_w$ [m/s]. We rewrite Eq. (57), using Eq. 29 as

$$J_s = BC_f R_{obs} e^{J_w/k_f}$$

which implies that $J_s$ increases exponentially with respect to $J_w$. Note that the solute flux must be equal to the permeate concentration multiplied by the permeate flux:

$$J_s = C_p J_w = C_f (1 - R_{obs}) J_w$$
Rigorously, $J_s$ in Eq. (58) indicates the solute flux through the membrane interior driven by the external concentration difference, $C_m - C_p$. Eq. (59) is based on the global mass balance implying that the solute molecules are uniformly mixed in the permeate stream after they have passed through the membrane.

2.3.3. Parameter estimation

**Solvent permeability.** The solvent permeability $A$ is an intrinsic material constant of a specific membrane and so needs to be experimentally measured. When the feed stream of zero concentration ($C_f = 0$) is filtered using an RO membrane, we have

$$A = \frac{J_0}{\Delta P}$$

where $J_0$ indicates the permeate flux of zero feed concentration. Using pure water, a series of filtration experiments can be conducted to measure $J_0$ with respect to $\Delta P$ as schematically shown in Fig. 5. The slope of the flux vs. pressure line can be calculated using a simple linear regression method to calculate the most probable $A$.

**Solute permeability.** Here, we simply assume that $B$ is also a constant within typical ranges of the solute concentration and applied pressure of normal RO processes. From Eqs. (53), (58) and (59), we obtain:

$$R_{obs}e^{J_w/k_f} = \frac{A\Delta P - J_w}{A\pi_f} = \frac{(1 - R_{obs}) J_w}{B}$$

which leads to

$$\frac{B}{A} = \frac{\pi_w J_0}{J_0 - J_w}$$

where $\pi_p = \pi_f (1 - R_{obs})$ is the osmotic pressure of the permeate stream and $J_0 - J_w$ indicates the permeate flux lost from the pure water flux $J_0$ due to the concentration polarization.

**Low flux limit.** When the permeate flux is low due to small effective pressure, the following approximations can be made. The intrinsic rejection $R_{int}$ converges to the observed rejection, $R_{int} \rightarrow R_{obs}$, because the CP must be negligible on the membrane surface $C_m \rightarrow C_f$, and hence $\pi_m \rightarrow \pi_f$. The solute flux is

$$J_s = C_p J_w = B_0 (C_f - C_p)$$

which gives

$$B_0 = J_w \frac{1 - R_{obs}}{R_{obs}}$$

where the subscript 0 indicates no or negligible concentration polarization. Then, $B$ of Eq. (61) can be expressed as:

$$B = B_0 e^{-J_w/k_f}$$

If $J_w/k_f \ll 1$, then $B$ converges to $B_0$ of the dilute limit.
Mass transfer coefficient. In system design and performance evaluation of RO processes, estimation of the mass transfer coefficient \( k_f \) is of great importance. A number of experiments can be conducted and accumulated data can be used to create empirical correlations for later use. Here, \( k_f \) can be represented using the solvent flux Eq. (53) and the solute flux Eq. (58), which are

\[
\frac{1}{k_f} = \frac{1}{J_w} \ln \frac{J_w^0 - J_w}{A\pi f R_{obs}} \quad (66)
\]

and

\[
\frac{1}{k_f} = \frac{1}{J_w} \ln \frac{1 - R_{obs}}{BR_{obs}} \quad (67)
\]

respectively. Values of \( k_f \) estimated using the above two equations should be comparable within a tolerable error.

2.3.4. Empirical correlations

When a feed solution is physico-chemically characterized and a module geometry is given, the crossflow speed \( v \) is almost the only controllable parameter to change the mass transfer coefficient \( k_f \). For dimensionless analysis, Sherwood number is represented as a function of Reynolds and Schmidt numbers and the aspect ratio of the channel geometry. (See Appendix A.2 for details.) Table I shows exponent values of \( a, b, c, \) and \( d \) in Eq. (A.9). For laminar flow, \( a \) of a rectangular channel is slightly higher than that of a cylindrical tube, while all other exponents are equally \( 1/3 \). Influences of Re, Sc, and module geometry on the \( k_f \) must be similar in cylindrical and rectangular channels and \( a \) represents the effect of the cross-section shape. For turbulent flow, \( a, b, \) and \( c \) are same for the cylindrical and rectangular channels and interestingly \( d = 0 \). Due to the complex nature of the turbulent flow field, the effect of hydraulic diameter vanishes, as the wetted surface area in the turbulence fails to provide a controllable impact on the mass transfer.

2.3.5. Long membrane modules

Fig. 6 shows a schematic of crossflow RO filtration. For a short membrane, the retentate concentration is

\[
C_{c} = \frac{C_f - C_{p}Y}{1 - Y} \quad (68)
\]

which implicitly neglects the concentration variation in the longitudinal direction, as shown in Fig. 2. For a long membrane, Eq. (68) holds its validity only if \( C_{p} \) is replaced by its length-averaged value:

\[
\overline{C}_{p} = \frac{1}{L} \int_{0}^{L} C_{p}(x) \, dx \quad (69)
\]
where $C_p(x)$ is a local permeate concentration at $x$ ($0 < x < L$). A local average concentration of $C_p(x)$ is denoted as

$$C_p' = \frac{1}{x} \int_0^x C_p(x') \, dx'$$

(70)

Then, the retentate concentration of Eq. (68) can be rewritten as

$$C_c = C_f - \bar{C}_p Y$$

(71)

where $Y$ is the (global) recovery ratio defined as $Y = Q_p/Q_f$.

*Mean osmotic pressure in the bulk phase.* To apply the solution-diffusion model for a long membrane module, a longitudinally mean osmotic pressure $\bar{\pi}$ needs to be used to calculate the mean transmembrane osmotic pressure: $\Delta\pi = \bar{\pi} - \pi_p$. A good approximation, especially for membrane array design, can be

$$\bar{\pi} = \frac{\pi_f + \pi_c}{2}$$

(72)

where $\pi_c = \pi(C_c)$. Note that Eq. (72) does not include the effect of the concentration polarization phenomena in the transverse direction. This forceful decoupling of mass balance equations in the transverse and longitudinal direction allows analytical solutions, which are later combined using empirical correlations. The mass transfer coefficient $k_f$, estimated using an empirical correlation, implicitly includes effects of the membrane length and the channel cross-section in addition to the transport mechanisms.

*Mulder’s theory.* Now we apply the same analysis at $x = l$. For a partial membrane of length $x$ from 0, $C_c$ and $C_p$ of a full membrane are replaced by their partial values $C_c'$ and $C_p'$, respectively, to give

$$C_c' = \frac{C_f - C_p' Y'}{1 - Y'}$$

(73)

where $Y'$ is a local recovery ratio for the partial membrane of length $x$. To solve this, we need an additional relationship such as

$$\frac{C_c'}{1 - R} = \langle C_c' \rangle$$

(74)

for which Mulder [34] assumed that

$$\langle C_c' \rangle = \frac{1}{Y'} \int_0^{Y'} C_c'(Y) \, dY$$

(75)
Substitution of Eq. (73) and (75) in (74) gives

\[ C'_c \cdot (1 - Y') = C_f - (1 - R) \int_0^{Y'} C'_c \, dY' \tag{76} \]

which is an integral equation for \( C'_c \). We differentiate Eq. (76) with respect to \( Y' \) to have

\[ \frac{dC'_c}{C'_c} = R \frac{dY'}{1 - Y'} \tag{77} \]

and integrate it such that

\[ \int_{C_f}^{C_c} \frac{dC'_c}{C'_c} = R \int_0^{Y'} \frac{dY'}{1 - Y'} \tag{78} \]

to obtain

\[ C_c = C_f \cdot (1 - Y)^{-R} \tag{79} \]

Substitution of (79) into (71) represents the mean permeate concentration:

\[ \bar{C}_p = C_f \frac{1 - (1 - Y)^{1 - R}}{Y} \tag{80} \]

represented as a function of \( C_f, R, \) and \( Y \). In this approach, \( Y \) implicitly includes impacts of \( A, A_m \) and \( \Delta P \), and \( R \) contains the rejecting role of \( B \).

Examples in the Appendix A.3 indicate that Mulder’s theory is valid when the rejection ratio is high, such as standard RO processes. The key equations (79) and (80) stem from the partial mass balance Eqs. (74) and (75). The solution-diffusion model uses specific permeability values of \( A \) and \( B \), to iteratively calculate the permeate concentration. As the CP is incorporated into the solution-diffusion model, \( C_m \) is considered higher than \( C_f \), but does not explicitly include variation of \( C_p \) in the longitudinal direction (from the inlet to the exit of the membrane module). An empirical correlation for the mass transfer coefficient \( k_f \) implicitly includes the length-averaged dimensionless numbers, and perhaps so does \( C_m \). Therefore, combination of the solution-diffusion model and \( k_f \) estimated using an empirical correlation is conceptually equivalent to Mulder’s intuitive assumption:

\[ \frac{\bar{C}_p}{1 - R} = \frac{1}{Y'} \int_0^{Y'} C'_c(Y) \, dY \]

Usually, vendors provide a rejection ratio for a membrane, measured at a reference condition, which in this case can be used as an intrinsic constant similar to \( A \) or \( B \). Mulder’s theory allows us to practically estimate the product permeate concentration using \( R \) and \( Y \) without dealing with specific transport models.

In section 2.1, a membrane is characterized using ten variables. Of these, six variables of \( A, B, A_m, \Delta P, C_f \) and \( Q_f \) usually are known. The four remaining ones
are calculated using the same number of equations, which are global mass balances of Eqs. (3) and (4), and solvent and solute fluxes of Eqs. (5) and (6), respectively. In Mulder’s approach, the membrane is treated as a black box of known $R$ and $Y$ so that the variable set includes eight elements \{$R, Y, C_f, Q_f, C_p, Q_p, C_c, Q_c$\} when $R$, $Y$, $C_f$, and $Q_f$ are known, then definitions of $R$ and $Y$, and global mass balance equations of solutes and solvent will be used to calculate the same total number of unknowns, such as \{$C_p, Q_p, C_c, Q_c$\}.

2.4. Coupled Governing Equations

An accurate governing equation without a forceful decoupling between the transverse and longitudinal directions is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial y} \left( D \frac{\partial C}{\partial y} \right) - u(y) \frac{\partial C}{\partial x} - v_w(x) \frac{\partial C}{\partial y} \quad (81)$$

where the solute diffusivity $D$ is often assumed to be constant and the longitudinal diffusion is discarded by indicating $\partial^2 C/\partial x^2 \ll \partial^2 C/\partial y^2$. Within the CP layer, the crossflow velocity is often represented as a linear shear flow with respect to $y$:

$$u(y) = \gamma y \quad (82)$$

where

$$\gamma = \left[ \frac{\partial u}{\partial y} \right]_{y=0} \quad (83)$$

is a shear rate on the membrane surface. The mathematical rigor of the coupled governing equation is closely related to the exponential dependence of the concentration near membrane surface on the permeate flux (see Eq. (27)). The only numerical solution seemed to be available for the 2D convection and diffusion of solutes on the membrane surface. A general solution of Eq. (81) was developed using Airy functions, but coefficients were obtained by numerical integrations. This work discovered that an inflection point of the concentration profile exists in the longitudinal crossflow direction. Even if these analytic approaches provide a fundamental insight of crossflow membrane filtration, they are still restricted to solute migration on the flat, slip-less surface in the linear shear field of Eq. (82). It is formidably difficult to develop an analytic solution of the 2D governing equation if one or some of the followings are considered: the presence of spacers, transient hydraulic pressure for pulsing, curved channels, and parabolic or nonlinear flow fields.

2.5. Fouling indexes and scaling potential

2.5.1. Modified fouling index (MFI) for colloidal fouling

When colloidal particles deposit on the membrane surface (typically, but not limited to, MF or UF membranes), the resistance-in-series model represents the permeate flux

$$J_w = \frac{\Delta P}{\eta \left( R_m + R_c \right)} \quad (84)$$
where $R_c$ is the resistance of the cake layer, i.e., temporarily or permanently built deposit layer of solid materials such as nano- or colloidal particles, (deformable) macromolecules or combined forms. In the dead-end filtration or at the initial stage of the crossflow filtration, $R_c$ continuously increases with respect to time. Moreover, often causing noticeable declining trends of the permeate flux, the specific cake resistance is defined as

$$r_c = \frac{R_c}{\delta_c} \quad (85)$$

which is independent on the cake thickness $\delta_c$ if the cake layer has a uniform mass density. In principle, the specific resistance is an inverse of the hydraulic permeability $\kappa$, i.e., $r_c = \frac{1}{\kappa}$, which is generally a function of particle size, particle shape, and cake porosity. If particulate materials are perfectly removed by a membrane, the amount of particle mass transported from the bulk (feed) phase to the membrane surface is equal to the particle mass accumulated on the membrane surface, which is mathematically written as

$$\phi_f V = \phi_c A_m \delta_c \quad (86)$$

where $\phi_f$ and $\phi_c$ are particle volume fractions in the feed solution and of the cake layer, respectively, and $V$ is the permeate volume, i.e., the solvent volume passed through the membrane having the surface area $A_m$. Substitution of (86) in (85) gives

$$R_c = \alpha V \quad (87)$$

where $\alpha = \frac{\phi_f r_c}{\phi_c A_m}$ is the proportionality between the cake resistance and the permeate volume. Eq. (87) indicates that the cake resistance increases as water is filtered by the membrane. By definition, the permeate flux is written as

$$J_w = \frac{1}{A_m} \frac{dV}{dt} \quad (88)$$

as it is proportional to the volume of produced solvent per unit time, i.e., $dV/dt$. Substitution of (87) and (88) in (84) provides

$$\frac{1}{A_m} \frac{dV}{dt} = \frac{\Delta P}{\eta (R_m + \alpha V)} \quad (89)$$

which is simply the first order ordinary differential equation of the filtered volume $V$, rewritten as

$$\eta (R_m + \alpha V) dV = \Delta P dt A_m \quad (90)$$

in an integrable form. Integration of this equation using the initial condition of $V(t = 0) = 0$ gives

$$t \frac{V}{V} = C_1 + C_2 V \quad (91)$$

where

$$C_1 = \frac{\eta R_m}{A_m \Delta P} \quad (92)$$
is the $y$-intercept of $t/V$ versus $V$ plot and

$$C_2 = \frac{\eta f r_c}{2 \phi_c A_m^2 \Delta P} \equiv \text{MFI} \quad (93)$$

is the slope, which is defined as modified fouling index (MFI) \[38, 39\]. This MFI cannot be easily calculated using Eq. (93), because the cake volume fraction $\phi_c$ is neither known nor (easily) measurable and $r_c$ is a complex non-linear function of $\phi_c$.

Theoretical calculation of MFI is challenging, because $\phi_c$ strongly depends on inter-particle and particle-membrane interactions and $r_c$ is a complex, non-linear function of $\phi_c$.

2.5.2. Combined fouling index (CFI)

When the feed solution contains both salt ions of high concentration and colloidal particles, the permeate flux may be expressed as a combination of the osmotic pressure model and the resistance-in-series model:

$$J_w = \frac{\Delta P - \Delta \pi_m}{\eta (R_m + R_c)} \quad (94)$$

where $\Delta \pi_m (= \pi_m - \pi_f)$ is the transmembrane osmotic pressure difference in the pressure of CP. Consider that the cake layer exists inside the concentration polarization layer of salt ions, i.e., $\delta_p > \delta_c$, where $\delta_p$ is the thickness of the salt concentration polarization layer above the membrane surface. Then we define

$$\delta_s = \delta_p - \delta_c \quad (95)$$

which is the partial thickness of the concentration polarization layer above the cake layer, within which the tangential cross flow velocity is assumed to be negligible. The surface of the cake layer may provide the no-slip boundary condition, which is similar to the (bare) membrane surface without the particle deposition. Then, the mass balance Eq. (24) can be employed using the solute diffusivity changing with respect to $y$:

$$D = \left\{ \begin{array}{ll} D_0 & \text{for } \delta_c < y < \delta_p \\ D_0 \epsilon \tau & \text{for } 0 < y < \delta_c \end{array} \right. \quad (96)$$

where $\epsilon (= 1 - \phi_c)$ is the cake porosity and $\tau$ is the diffusive tortuosity. In Eq. (24), $dy/(C - C_p)$ is multiplied on both sides to give

$$\int_{C_m}^{C_f} \frac{dC}{C - C_p} = -\int_0^{\delta_c} \frac{J_w \tau}{D_0 \epsilon} dy - \int_{\delta_c}^{\delta_p - \delta_c} \frac{J_w}{D_0} dy \quad (97)$$

which is solved as

$$\ln \frac{C_f - C_p}{C_m - C_p} = -\frac{J_w}{D_0} \left( \frac{\tau}{\epsilon} \delta_c + \delta_s \right) \quad (98)$$
The cake volume fraction \( \phi_c \) is often assumed to be a random close packing ratio of 0.64 \([40, 41]\), and the diffusive tortuosity \( \tau \) is in principle greater than 1.0, varying with \( \phi_c \) and the internal structure of the cake layer. For a thick cake layer, the concentration polarization above the cake layer does not significantly contribute to the permeate flux. So, one can approximate Eq. (98) by removing \( \delta_s \) as

\[
\frac{C_m - C_p}{C_f - C_p} = \exp \left( \frac{J_w \delta_c}{D_0 \epsilon / \tau} \right) = e^j
\]

where we define a dimensionless permeate flux

\[
j = \frac{J_w}{k_c}
\]

and

\[
k_c = \frac{D_0}{\delta_c \tau / \epsilon}
\]

which is interpreted as the diffusive mass-transfer coefficient of solute ions in the cake layer of porosity \( \epsilon \). The denominator of Eq. (101), \( \delta_c \tau / \epsilon \), can be considered as the effective path length of diffusing solutes within the cake layer, which is longer than that in the void space.

Substitution of Eq. (99) in (94) gives the final equation to solve for \( j \):

\[
j = \frac{\Delta P - \pi_f R_{\text{obs}} e^j}{k_c \eta (R_m + R_c)}
\]

Similar to the previous case, we assume \( j < 1 \) to use

\[
e^j = 1 + j + O(j^2)
\]

and substitute Eq. (103) with (102). We then replace \( j \) by \((k_c A_m)^{-1} dV/\text{dt}\) and use Eq. (87) to give

\[
\eta \left[ R_m + \frac{\pi_f R_{\text{obs}}}{k_c \eta} + \alpha V \right] dV = (\Delta P - \pi_f R_{\text{obs}}) A_m \text{d}t
\]

Integration of both sides using an initial condition of \( V = 0 \) at \( t = 0 \) provides

\[
t = \left( \frac{\eta R_m}{A_m dP} \right) \left( \frac{1 + \hat{\pi}_f J_{\text{w0}}}{1 - \hat{\pi}_f} \right) V + \left( \frac{\eta \phi f r_c}{2 \phi_c A_m^2 \Delta P} \right) \frac{1}{(1 - \hat{\pi}_f)} V^2
\]

simplified to

\[
\frac{t}{V} = C_1 \left( \frac{1 + \hat{\pi}_f J_{\text{w0}}}{1 - \hat{\pi}_f} \right) + \frac{\text{MFI}}{(1 - \hat{\pi}_f)} V
\]
where

\[ \hat{\pi}_f = \frac{\pi_f R_{\text{obs}}}{\Delta P} \]  

(106)

indicates the ratio of the osmotic pressure of the net concentration \( \pi_f R_{\text{obs}} \) to the applied pressure \( \Delta P \). Now, we can take the proportional constant of \( V \) in Eq. (105) to define the combined fouling index (CFI) as

\[ \text{CFI} = \frac{\text{MFI}}{1 - \hat{\pi}_f} \]  

(107)

The absence of the salt ions in the feed stream can be considered by setting \( \hat{\pi}_f = 0 \) which makes CFI converge to MFI and Eq. (105) equal to (91). In this case, applications are limited to MF or UF processes. The fouling tendency of RO desalination can be quantified using the CP factor \( \beta \), defined as

\[ \beta = \frac{C_m}{C_f} \]  

(108)

which can be calculated using the measured permeate flux \( J_w \) and the empirically-determined mass transfer coefficient \( k_f \) in Eq. (27). In addition to \( \beta \), CFI can be used to estimate the combined fouling tendency in the presence of both ionic and particulate species. Note that CFI is always larger than MFI. For example, if \( \Delta P \) is set as twice seawater osmotic pressure \( \pi_{\text{sw}} \), then we calculate \( \hat{\pi}_f = 2\pi_{\text{sw}}/\pi_{\text{sw}} = 2 \) and CFI = 2 MFI using Eq. (107). Related experimental and modeling studies can be found elsewhere [42-45].

3. Concluding Remarks

In this study, I briefly reviewed the fundamentals of reverse osmosis processes, based on the solution-diffusion model. Specific variations of output variables such as concentrations and outflow rates of the permeate and brine streams are characterized with respect to the input and operating parameters. Transverse variations of the solute concentration are reviewed by solving the decoupled convection-diffusion equation. Mulder’s theory is discussed to explain the longitudinal variations of permeate flux, which primarily controls the rejection and recovery ratios. The solution-diffusion model was also reviewed using principles and concepts of statistical mechanics. Finally, the degree of combined fouling (by both ionic solutes and particulate materials) is quantified using a novel combined fouling index (CFI) as an extension of the modified fouling index (MFI).

In environmental engineering, which is the discipline closest to mother nature, a holistic understanding of transport phenomena at the basic level of thermodynamics, statistical mechanics, and fluid mechanics is as important as practically dealing with designing, optimizing, and maintaining specific processes. Hopefully, this incomplete manuscript can be a stepping stone for future membrane engineers, who may resolve the impending global water shortage.
Figure 1. (a) Assembling film packages in prototype desalination cell and (b) life test assembly (Figure 3 and 8 of Ref. [1], respectively. Reprinted.)

Figure 2. A schematic of the RO process.
Figure 3. Theoretical causes and effects in basic RO modeling. Parameters used are $T = 25^\circ C$, $A_m = 150 \text{ m}^2$, $A = 1.36 \times 10^{-7} \text{ m/s psi}$, $B = 5.0 \times 10^{-8} \text{ m/s}$, $Q_f = 864 \text{ m}^3/\text{day}$, $C_f = 35 \text{ g/l}$, $\Delta P = 800 \text{ psi}$. Three variables of $\Delta P, Q_f$ and $C_f$ are selected as independent variable in the first, second and third rows, respectively. Variations of $C_p, Q_p$ and $C_c$ are calculated with respect to one independent variable while the rest two are kept constant.
Figure 4. Schematic of concentration profile across the membrane in the crossflow.

Figure 5. Schematic of the pure water flux with respect to the applied pressure.
Figure 6. RO schematic with local balance.

Table 1. Exponents of the mass transfer coefficient in terms of channel geometry and flow regions.
Appendix A. Appendix

Appendix A.1. Proof of Eq. (27)

The permeate flux \( J_w \), the permeate concentration \( C_p \), and the solute diffusivity \( D \) are constant. Eq. (24) is rewritten, using the net or excessive concentration \( C' = C - C_p \), as

\[
D \frac{dC'}{dy} = -J_w C' \tag{A.1}
\]

Because only \( C' \) is a sole function of \( y \), one rewrites Eq. (A.1) as

\[
\frac{dC'}{C'} = - \frac{J_w}{D} dy \tag{A.2}
\]

Integration of Eq. (A.2) gives

\[
\ln C' = - \frac{J_w}{D} y + \text{constant} \tag{A.3}
\]

of which the constant is determined using the boundary condition of Eq. (25):

\[
\ln [C_m - C_p] = \text{constant} \tag{A.4}
\]

The boundary condition of Eq. (26) on the top of the CP layer provides

\[
\ln [C_f - C_p] = - \frac{J_w}{D} \delta_p + \text{constant} \tag{A.5}
\]

Substitution of Eq. (A.4) in (A.5) generates

\[
\frac{C_m - C_p}{C_f - C_p} = \exp \left[ + \frac{J_w}{D/\delta_p} \right] \tag{A.6}
\]

in which the solute diffusivity per CP layer thickness, \( D/\delta_m \), refers to the mass transfer coefficient \( k_f \) of the same dimension of the permeate flux \( J_w \). Substitution of Eq. (A.4) in (A.3) gives the solute concentration \( C(y) \) as a function of the distance from the membrane surface \( y \):

\[
\frac{C(y) - C_p}{C_m - C_p} = \exp \left[ - \frac{J_w y}{D} \right] \quad \text{for} \quad 0 < y < \delta_p \tag{A.7}
\]

The concentration exponentially increases from \( C_f \) at the CP layer boundary to \( C_m \) on the membrane surface.
Appendix A.2. Dimensionless number analysis

The performance of a membrane is typically estimated using the recovery and rejection ratios, which are primarily determined by $A$ and $B$, respectively, which are intrinsic material properties of the membrane. On the other hand, the mass transfer coefficient $k_f$ is strongly dependent on fluid dynamics and module geometry. In engineering and applied sciences, dimensionless numbers are often used to represent correlations between representative physical quantities. The Sherwood number ($Sh$) includes the mass transfer coefficient such as

$$Sh = \frac{k_f d_h}{D} = \frac{\text{convective mass transfer rate}}{\text{diffusive mass transfer rate}}$$

implying the significance of the convection over the diffusion of solutes, where $d_h$ is the hydraulic diameter. The Sherwood number is often represented as a function of Reynolds (Re) and Schmidt (Sc) numbers:

$$Sh = a \text{Re}^b \text{Sc}^c \left(\frac{d_h}{L}\right)^d$$

where $L$ is the membrane (or channel) length, and $a - d$ are constants. Here, $d_h/L$ can be considered as the aspect ratio of the flow channel. The Reynolds number measures a ratio of inertial to viscous forces for given flow conditions, which is defined as

$$Re = \frac{vd_h}{\nu} = \frac{v \rho d_h}{\eta}$$

where $v$ is the flow speed, $\rho$ is the fluid density, and $\eta$ and $\nu$ are the absolute and kinematic viscosities, respectively. In the case of flow through a straight pipe with a circular cross-section, fluid motion will be laminar at $Re < 2000$, whereas at $Re > 4000$, the flow is turbulent. The Schmidt number represents a ratio of convective to diffusive mass transport:

$$Sc = \frac{\nu}{D}$$

Appendix A.3. Application of Mulder’s theory to Seawater Desalination

An RO desalination process has a feed water of 35,000 ppm and the rejection ratio of the selected membrane is reported by a vendor as 99.00%. If the process is operated for 60% recovery, then the permeate concentration is predicted as

$$C_p = C_f \frac{1 - (1 - 0.6)^{1-0.99}}{0.6} = C_f \times 0.01520 = 532.06 \text{ ppm}$$

If so, one calculates

$$1 - \frac{C_p}{C_f} = 0.9848$$
which is close enough to 0.9900. If we replace the rejection by 40% (such as that of nanofiltration), then we calculate

\[
\bar{C}_p = C_f \frac{1 - (1 - 0.6)^{1-0.40}}{0.6} = C_f \times 0.7048 = 24670.33 \text{ ppm} \tag{A.14}
\]

and

\[
1 - \frac{\bar{C}_p}{C_f} = 0.2951 \tag{A.15}
\]

which is different from 40%.

References


