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Reverse Osmosis Process Membranes Modeling – A Historical Overview

Djamel Ghernaout[1, 2]

[1]Department of Chemical Engineering, College of Engineering, University of Hail, Ha'il, Saudi Arabia

[2]Department of Chemical Engineering, College of Engineering, University of Blida, Blida, Algeria

Email address:

djamel_andalus@hotmail.com

Abstract: This paper presents an overview to the state-of-the-art area of mathematical modeling for reverse osmosis (RO) process. As a liquid-solid process, RO constitutes a valuable and vital physical solution for seawater desalination, wastewater depollution, and water treatment comparatively to the largely controversial and polluting chemical processes such as chlorination and coagulation/flocculation. Great works are required in modeling of RO technique in order to obtain a complete and exhaustive model. Complicated and varying raw water qualities and quantities parameters through time and space are rendering RO modeling hard. Be facing the increasing pollution levels and trying to satisfy the drinking water guidelines, RO membrane modification is often required. This situation made modeling this highly dynamic process more difficult to accomplish.

Keywords: Reverse Osmosis (RO), Thin-Film Composite (TFC), Desalination, Water/Wastewater Treatment, Seawater, Brackish Water, Concentration Polarization (CP)

1. Introduction

Invented 60 years ago, reverse osmosis (RO) became a frequent unit operation in chemical and environmental engineering plants [1-4]. Nowadays, this membrane process is occurring in a larger interval of industrial applications such as desalination of seawater and brackish water, treatment of municipal and industrial wastes, concentration of food products, production of ultra-pure water for several applications comprising the semi-conductor industry, and recovery of important materials in chemical and petrochemical industries [5-12].

RO is an interesting process since it is simple, it can be used for a wide interval of issues in diverse fields, it is economically competitive, and it needs no phase variation [13-15]. The last characteristic is especially crucial for solutions which are responsive to heating, such as food products and pharmaceutical materials [5, 16-18].

The new idea, which conducted to RO, begun in the early 1950's at the University of California at Los Angeles (UCLA), where Samuel T. Yuster imagined the concept of utilizing the Gibb's adsorption equation as a road map to discover methods

for making fresh water from brackish water and seawater [7, 19, 20]. Following Gibb's equation, a comparatively pure water film should occur at the interface of brine and air (or any other hydrophobic surface) which may be skimmed off and, consequently, fresh water may be made. Initially, the implementation of the concept failed until solid-liquid (rather than liquid-gas) interface was studied [21]. The initial idea was to allow pure water create at the solid-liquid interface and then skim the water off by pushing the interfacial water to flow, under an elevated pressure, through the pores of the solid. At this period, the first victorious experiment was realized utilizing a flat plastic film, supported by a porous plate, in 1958 at UCLA [5, 19, 22, 23]. On one's own, approximately the same period, Breton and Reid performed the first effective RO experiments utilizing cellulose acetate membranes and seawater, at the University of Florida [24, 25]. Nevertheless, at that period, the permeation flux of water was very low (approximately a few drops per week) and, consequently, the process was not convenient for industrial application. The advance, which pushed RO to be commercially viable, arrived

in 1958 when Loeb and Sourirajan produced the first asymmetric cellulose acetate membrane [26]; the membrane was not a uniform membrane as previously but was produced of a thin skin film, which was as dense as the precedent homogeneous membranes, and a porous support film. In the Loeb-Sourirajan membrane, important fluxes may be achieved because the flow resistance, in the asymmetric membranes, was much lower than in the uniform membranes [5, 27-30].

To report conveniently the efficiency of a RO membrane, mathematical models are required [31, 32]. These mathematical equations may be subsequently employed for convenient design of RO units [33]. This need has conducted to the expansion of some transport models [34]. The main goal of a transport model is to describe the membrane efficiency, habitually shown as permeation flux and separation (percentage of solute removal from feed solution), to the conditions in operation (such as pressure or feed concentration) or the driving forces (frequently pressure and concentration gradients) through some coefficients (known as phenomenological transport coefficients) which comprise the model parameters [35, 36]. The coefficients (or the parameters) have to be established from experimental information. The triumph of a model can be quantified in matter of the capacity of the model to show mathematically the information with coefficients (or parameters) that are rationally constant through the interval of working conditions. Finally, the model with the established transport coefficients can illustrate the efficiency of a membrane through a large interval of working conditions. This capacity to anticipate the efficiency is the real potential of a transport model. This can be employed, partially, to avoid the elevated costs of experimentation. Integrated with a research program in membrane manufacturing, this may conduct to better conception standards for customizing producing membranes, and joined with a process design program may conduct to a more rational scale-up for RO systems [5, 37, 38].

This review presents a global view on the state-of-the-art area of mathematical modeling for RO process.

2. First Principles of Membrane Process

This section covers the primary definitions and concepts employed usually in RO writings [5].

2.1. Osmosis, Osmotic Pressure and RO

While a semi-permeable membrane (permeable to solvent but not to solute) is put in the midst of two compartments, one containing pure solvent and the other containing a solution (the solvent plus a solute), the solvent penetrates over the membrane to the solution part. This process, which is named "osmosis" (Figure 1(a)), occurs since the system looks for thermodynamic equilibrium. The chemical potential of the pure solvent is bigger than that of the solvent in the solution part thus solvent flows to the solution part to tend to recover equilibrium [5, 39, 40].
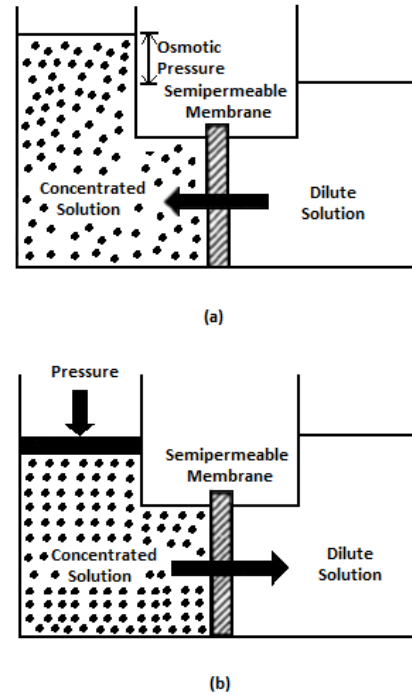

Figure 1. (a) Osmosis, osmotic pressure, and (b) RO [6].

In a device, such as shown in Figure 1, the equilibrium is obtained when there is no net solvent flow over the membrane. The pressure head produced on the solution part is called the "osmotic pressure" (Figure 1(a)), which is a thermodynamic characteristic of the solution and independent of the membrane. When a pressure bigger than the osmotic pressure is imposed to the solution part, augmenting the chemical potential, the solvent flow moves back from the solution part to the pure solvent part; the process is called the "reverse osmosis" or RO as illustrated in Figure 1(b) [6]. For an actual membrane, some solute may be displaced over the membrane and, consequently, the osmotic pressures of the solutions on both parts of the membrane have to be taken into account in modeling. An "efficient pressure driving force" from one side to the other of the membrane can be defined as the applied pressure difference, ΔP, minus the osmotic pressure difference, $\Delta \pi$, from one side to the other of the membrane. For most models, the solvent flux, N_B, is looked to be proportional to the effective pressure driving force, $(\Delta p - \Delta \pi)$ [5, 41, 42].

The osmotic pressure of a solution, π, is linked to the mole fraction and the partial molar volume of the solvent as [43]:

$$\pi = -\frac{RT}{v_B} ln X_B \tag{1}$$

For dilute solutions, Eq. (1) is reduced to van't Hoff equation [7, 43]:

$$\pi = C_A RT \text{ for nondissociable solutes} \tag{2}$$

$$\pi = (v^+ + v^-) C_A RT \text{ for dissociable solutes} \tag{3}$$

It is more suitable to utilize experimental values of osmotic pressures, which can be obtained for diverse solutions, from different references [5, 7, 44, 45].

2.2. Driving Forces for RO

In RO, the important driving forces are pressure and concentration gradients which conduct to permeation flux of solvent and solute, respectively. The cross effect of solute concentration driving force on solvent flux is symbolized by the osmotic pressure term in the solvent flux equation (see the "effective pressure driving force" in Section 2.1). The cross effect of pressure driving force on solute flux is usually low, for high separation membranes, and is frequently ignored; at what time taken into account this influence is termed by the Staverman (or reflection) coefficient, σ [46]. At what time the Staverman coefficient is considered, the equation of solvent flux is formulated, in most models [47, 48], as:

$$N_B = A[\Delta P - \sigma(\pi_2 - \pi_3)] \qquad (4)$$

where A is the solvent permeability coefficient [5].

The Staverman coefficient, σ, is a separation property of the membrane which may take values in the interval $0 \leq \sigma \leq 1$. The closer the σ is to 1, the greater the membrane separation; consequently, $\sigma = 0$ identifies a membrane with very small solute refusal, and $\sigma = 1$ identifies a membrane with total solute refusal [5].

2.3. Membrane Efficiency and Concentration Polarization (CP)

Membrane efficiency is frequently described in matter of "permeation flux" and "separation" [49]. The flux is the rate of material conveyed per unit membrane area, and separation is the fractional concentration decrease of solute from feed stream (i.e., the high-pressure side solution) as juxtaposed with permeate stream (i.e., the low-pressure side solution) [5].

Separation, f (which is occasionally named "rejection" or "retention" in some references), is described in matter of the feed bulk molality, m_{A1}, and the permeate molality, m_{A3} [7]:

$$f = \frac{m_{A1} - m_{A3}}{m_{A1}} \qquad (5)$$

For fairly dilute solutions, the molal concentration, m_{Ai}, may be estimated by molar concentration, C_{Ai}, and Eq. (5) be formulated as [5]:

$$f = \frac{C_{A1} - C_{A3}}{C_{A1}} \qquad (6)$$

On the other hand, separation may be described in matter of the concentration of the boundary-film solution just outside the membrane on the high-pressure part, C_{A2}. This separation, $\acute{f}$, named the "theoretical separation", is formulated, for quite dilute solutions, as [5]:

$$\acute{f} = \frac{C_{A2} - C_{A3}}{C_{A2}} \qquad (7)$$

The boundary-layer concentration, C_{A2}, can vary from the feed bulk concentration, C_{A1}, because of a process named "concentration polarization" (CP) [50]. The polarization influence takes place since as solute is rejected by the membrane the solute concentration augments close the

membrane; this situation, which is known as the "solvent-membrane affinity" situation, has been represented in Figure 2. Compared to the solvent-membrane affinity situation is the "solute-membrane affinity" situation in which the solute molecules are caught, rather than refused, by the membrane; this situation is illustrated in Figures 3 and 4 for positive and negative separations, respectively. At steady state, C_{A2} does not change as a function with time and the "film theory" is used to illustrate the CP influence [51-53]. A mass balance for solute through the membrane gives a form of Fick's first law which by integration conducts to [5]:
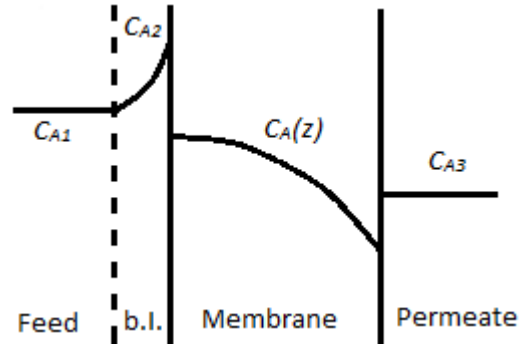
Figure 2. Partitioning influence in a solvent-membrane affinity system (e.g., NaCl-water-cellulose acetate membrane) [5].
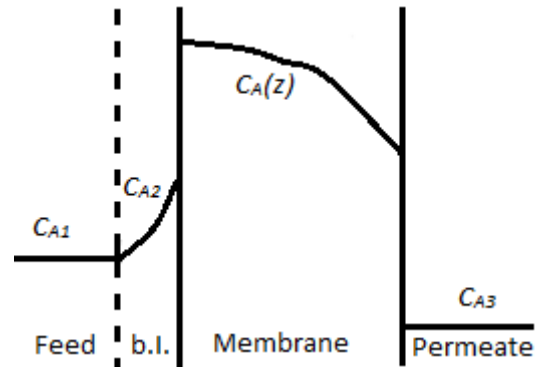
Figure 3. Partitioning influence in a solute-membrane affinity system with positive separation (e.g., toluen water-cellulose acetate membrane) [5].

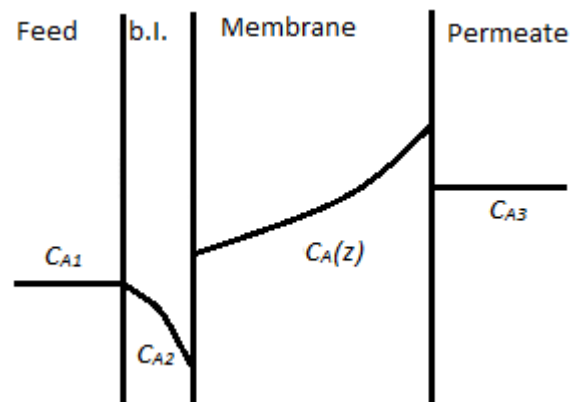**Figure 4.** Partitioning influence in a strong solute-membrane affinity system with negative separation (e.g., p-cholorophenol-water-cellulose acetate membrane) [5].

$$C_{A2} = C_{A3} + (C_{A1} - C_{A3})e^{(J_v/k)} \qquad (8)$$

where k is the mass transfer coefficient, a characteristic of the boundary layer [7]. As mixing on the elevated-pressure part of the membrane is augmented, Eq. (8) tells in advance that the mass transfer coefficient augments decreasing the polarization influence (i.e., C_{A2} moves toward C_{A1}). When mixing is infinite (i.e., $k \rightarrow \infty$) $\acute{f}$ moves toward f; consequently, $\acute{f}$ is the theoretical separation that would be metered with ideal mixing on the elevated-pressure part of the membrane [7]. CP is an unwelcome influence [54]. As the polarization effect augments larger the boundary-layer concentration elevates, the osmotic pressure elevates, and, consequently, the effective pressure driving force $(\Delta p - \Delta \pi)$ reduces; therefore the solvent flux reduces (see Eq. (4)) [5].

The mass transfer coefficient, k, depends on feed flow rate, cell geometry, and solute system. Generalized correlations of mass transfer coefficient propose that the Sherwood number, Sh, is a function of Reynolds, Re, and Shmidt, Sc, numbers [7, 55]:

$$Sh = \acute{a}Re^{b}Sc^{1/3} \tag{9}$$

where $\acute{a}$ and $\acute{b}$ are parameters to be evaluated by experiments [5].

For a constant flow rate and cell configuration, Eq. (9) suggests that k changes as a function of solute diffusivity to the 2/3 power, because the Reynolds number wipes out and the Schmidt number is inversely proportional to the solute diffusivity. Reformulating Eq. (9) comparatively to a reference solute at the identical working states produces [7]:

$$k = k_{ref} \left(\frac{D_{AB}}{D_{AB,ref}} \right)^{2/3} \tag{10}$$

As a result, if k_{ref} is known for a reference solute, therefore k for any other solute can be evaluated using Eq. (10) if the working states are identical [5].

A significative correlation in RO transport principles, which is employed in several transport models, is the correlation between the solute and solvent fluxes. These two fluxes are linked to the permeate concentration by a global mass balance as [5]:

$$C_{A3} = C \frac{N_A}{N_A + N_B} \tag{11}$$

3. RO Membranes and Membrane Modules

First RO membranes were uniform (i.e., with an isotropically dense film); for this reason, water permeation flux was exceptionally low because of the big flow resistance given by the homogeneous thickness of the membrane [5, 25, 56].

The triumph of the RO technique is attributed to a big range to the expansion of an "asymmetric membrane", initially advanced by Loeb dand Sourirajan [26]. An asymmetric membrane is manufactured to produce a relatively ultrathin, dense surface film suported underneath by a much thicker, porous film. The asymmetric structure is a direct result of the casting technique employed. While a polymer solution is cast on a flat surface, the evaporation of the solution gives a surface skin. Ulterior gelation in cold water fixes the structure; the porous film is constituted by the substitution of the solvent by the nonsolvent water [7]. Scanning electron microscopy specifies that three films occur in an asymmetric membrane: a relatively dense surface skin, a transition film, and a porous support film [57]. The transition film is in-between in both density and position comparatively to the other two films. The great part of the resistance to mass transfer over the membrane occurs in the surface skin. Consequently, it can be supposed that the membrane efficiency is a function mostly of the chemical nature and physical structure of the surface skin [5, 58, 59].

To a certain degrebrevity and completeness. new generation of membranes, which is a member of the family of asymmetric membranes, are the "thin-film composite" (TFC) membranes [60-62]. These membranes possess an alike composition to asymmetric membranes except that the films are manufactured one by one: the porous support is manufactured before anything else, from one polymer material, and a thin layer of a different polymer is covered (usually by interfacial polymerisation) on the porous substrate [5, 63, 64].

Concerning the skin film, the fundamental interrogation is if it is porous. Scanning electron microscopy has shown that ultrafiltration membranes are obviously porous; however, while it concerns the extremely fine structure of RO membranes, no pores have been identified. The presence or absence of pores in RO membranes may not be shown by nowadays knowledge [5]. This is the heart of the discussion in which certain transport models suppose the membrane to be porous and some suppose the membrane as non-porous; certain models, which are frequently based on irreversible thermodynamics (IT), suppose no specific membrane composition or transport phenomena [5, 65].

One tradely triumphant type of TFC membrane is the aromatic polyamide FT30 membranes produced by FilmTec Corporation [63, 66-69]. The FT30 membrane comprises three portions: an ultrafin, skin film of ∼ 0.25 μm thick; a microporous support film of polysulfone (∼50 μm thick); and a polyester carrier web with extremely big pores and a thickness of ∼ 125 μm. The chemical material of the skin film is a crosslinked aromatic polyamide with some anionic functionality (i.e., negative charges). The skin film in the FT30 membrane posses a thickness some times that in other TFC membranes [66]; this forces the membrane to be much more resistant to mechanical and oxidizing damage. The membrane may be employed in a large interval of pH: ∼3-11 for continous runnings and 1-13 for short-term runnings. This lets the membrane to be washed with strong acid and base solutions at temperatures reaching 50°C. One more crucial property of FT30 membranes is the durability at elevated temperatures; experiments have been performed up to 85°C [66]. The FT30 membranes have illustrated reasonable resistance to chlorine aggression, an experiment missed by most of the other noncellulosic RO membranes. The minimum

rate of oxidation aggression has been detected in the pH interval of 5-6 for small durations of time [69]. Fixed exposure or elevated chlorine concentrations (> 5 ppm) will demolish FT30 membranes quickly. Seawater experiments (35 000 ppm total dissolved salts (TDS)) have demonstrated salt refusals of ~99.0 to 99.2 percent for spiral-wound elements of FT30 membranes at 5.5×10^5 Pa pressure and 25°C temperature; the corresponding permeation fluxes of ~1.04×10^{-5} m^3/m^2 s have been mentionned at these situations [68]. For brackish water solutions (2000 ppm TDS), fluxes of ~0.75×10^{-5} m^3/m^2 s and salt rejections of ~96 percent have been mentionned for 1.38×10^5 Pa pressure and 25°C temperature [5, 68, 70-72].

Two tradely crucial members of the family of FT30 membranes are the so-called SW30HR (Sea Water-High Rejection) and BW30 (Brackish Water) membranes. SW30HR is an elevated refusal membrane employed for seawater desalination, and BW30 is utilized for brackish water desalination. These two membranes are chemically identical but possess distinguished efficiency; the correct difference between these membranes is proprietary. Despite the elevated flux and elevated separation properties of TFC membranes, comprising the FT30 membranes, small effort has been performed to know the transport properties of these membranes [5].

Some technologies have been advanced to put a big membrane area into a relatively little volume, for industrial usage. The most well-known of these conceptions are: spiral wound, hollow fibre, and tubular. The proportional qualities of each of these conceptions is function of the specific use [5, 6, 73-77].

4. RO Transport Mechanisms and Models

In the last few decades, a big number of models and theories have been suggested to illustrate the transport mechanism of solute and solvent over RO membranes [5]. Some reviews may be found in the literature [8, 34, 78]. The models have been frequently suggested in order to illustrate the transport mechanisms in RO processes (for those models which suppose several types of transport mechanism in the membrane). However, large approval subsists concerning the mechanism. These models have been obtained from two distinct large approaches. The first group of models, named phenomenological, are frequently founded on IT where the membrane is considered as a black box in which comparatively steady processes appear near equilibrium [79, 80]. In these models, fluxes are linear combinations of forces in the system [5].

In the second group of models (which may be named the "mechanistic models"), a mechanism of transport is supposed and, appropriately, fluxes are linked to the driving forces that occur in the system. The general models can be partaged into general and electrokinetic models [81]. The general models can be put in an application for any type of solute; but, the electrokinetic modes apply only to electrolytic solution feeds.

From another viewpoint, the mechanistic models can be partaged into porous and non-porous membrane models. The transport models in the porous membrane group suppose that the membrane is porous, and those in the non-porous membrane group assumes the membrane is dense and not porous [5].

4.1. Transport Mechanisms

The mechanism of membrane transport in RO remains a matter of debate [5]. Some mechanisms have been proposed; these mechanisms are discussed shortly here.

4.1.1. Sieve Mechanism
This extremely easy idea of sieve-filtration affirms that membrane separation happens because of the difference between the molecular sizes of solute and solvent; the membrane pore size must be in the midst of the two molecular sizes [82]. The mechanism is excluded in RO because it may not illustrate systems such as sodium chloride-water in which the molecular sizes of the solute and water are approximately identical [5].

4.1.2. Wetted Surface Mechanism
Reid and Breton recognized that, because of wettability of membrane materials, water is sorbed into the membrane by hydrogen bonding [25]. The long chained water structure, blocking up the membranes pores, subsequently prohibits the solute transfer across the membrane [5]. The water thereafter permeates by diffusing from one wetted part to another.

4.1.3. Solution-Diffusion (SD) Mechanism
Following this mechanism, proposed by Lonsdale et al., the solute and solvent primarily dissolve in the dense skin film of a membrane and after that diffuse across the membrane; consequently, the solubilities and diffusivities of the solution component are of great significance [83]. Pore flow (i.e., convection [84]) is avoided in this mechanism. After that, Sherwood et al. enlarged the SD model by supposing some imperfections, or holes, on the membrane surface film which particpate to the pore flow of solute and solvent, which is famous as the Solution-Diffusion-Imperfection model [5, 85].

4.1.4. Preferential Sorption-Capillary Flow (PS-CF) Mechanism
At the opposite side to SD mechanism, previously, the PS-CF mechanism, primarily proposed by Sourirajan, supposes that the skin film of the membrane is porous [19]. Following this mechanism, the membrane transport is to a certain degree directed by surface phenomena, at the solution-skin film interface, and partialy by fluid transport over the micro-capillaries. The physicochemical characteristic of the solute-solvent-membrane surface system establishes which compound of solution is discriminatory sorbed by the membrane. As an example, for the system NaCl-water-cellulose acetate, in which the membrane possesses a low dielectric constant, the ions are repulsed by the membrane and a solute-free film of water is sorbed on the membrane. The pure water film is subsequently pushed to

flow across the capillaries under the system pressure. Once upon a time, Glueckauf had evaluated, using surface tension information, that the thickness of the pure water film is ~0.35 nm [5, 86, 87].

4.2. Transport Models

This section shortly presents certain significant transport models of RO. More information may be discovered in the literature [34, 78].

A small number of models have considered the membrane as a "black box" in which no mechanism has been supposed. Subsequently, the principles of IT have been put in an application to obtain equations for the membrane separation and flux. One of the concepts of IT is that the system may be partaged into a small subsystems in which local equilibrium may occur and consequently thermodynamic quantities may formulated for these subsystems. For systems that are not too distant from equilibrium, IT proposes logical formulas between forces and fluxes [5].

Onsager proposed that the fluxes and forces may be formulated by the following linear equations [88]:

$$J_i = L_{ii}F_i + \sum_{i \neq j} L_{ii}F_i ; \ i = 1, n \qquad (12)$$

where the fluxes, J_i, are linked to the forces, F_j, by the phenomenological coefficients, L_{ij}. For membrane systems, the driving forces may be linked to the pressure and concentration differences through the membranes, and the fluxes are solvent and solute permeate fluxes. Eq. (12) may be made easier to understand by supposing that cross coefficients are the same [88]:

$$L_{ij} = L_{ji} \ \text{for} \ i \neq j \qquad (13)$$

The above Onsager reciprocal relationship (ORR), Eq. (12), is acceptable if the system is near equilibrium, the linear laws (i.e., Eq. (12)) are acceptable, and the exact selection of fluxes and forces has been performed. For systems that are distant from equilibrium, as is frequently the situation in RO, Eq. (13) may not be exact. The veracity of the ORR has been treated by Soltanieh and Gill [34].

Two most important phenomenological transport models based on IT are discussed by [5].

5. Computational Fluid Dynamics (CFD) Modeling for Membrane Filtration

Noticing and measuring the flow and solute transfer inside the membrane system, particularly the concentration close to the membrane surface, is hard using experiments; therefore, analytical and numerical CFD solutions have been utilized to examine the hydrodynamics [89, 90]. Primarily analytical and numerical solutions were not able to adress spacerfilled membrane channels since it was difficult to construct such complex geometry in the model and they required to use facilitated or predefined velocity profiles [91, 92]. Several following researches have mentioned that spacers have a

crucial action in dictating velocity and concentration distribution within membrane channels; therefore, the primary models without spacers were restricted in their usage [93-95].

An additional facilitation in primary CFD modeling was that the permeate flow across the membrane (flux) was frequently neglected or placed as a constant number. By performing so, the reciprocal action enter the fluid flow and solute transport was neglected. This significated the models were incapable to assess a crucial property of membrane filtration and CP [90, 96-103].

6. Development of the Stagnant Film Model

As seen in Section 2.3, precise models for CP, the accumulation of solutes at the membrane–solution interface in RO tubes, are crucial for anticipating system efficiency [12]. Regardless of its empirical good results, several modeling approaches used in the deduction of the frequently-utilized stagnant film model appear to restrict the model's usage to actual situations. Moreover, several subsisting models for CP utilize an average mass transfer coefficient with a local mass transfer driving force, which conducts to inaccurate anticipations for the osmotic pressure at the membrane–channel interface. Rohlfs et al. decreased the Zydney-transformed governing equations for solute mass transfer to an analogous convective heat transfer problem [12]. They then applied the principle of superposition to fit solutions from the heat transfer problem to the RO tube boundary conditions, producing a solution that exactly takes into account a local transport coefficient with a local mass transfer driving force. The finished relationships for RO element sizing and rating illustrates good accord with experimental information and gives a theoretical construction for CP modeling that considers the characteristic formation of the mass transfer boundary film not taken into account for by several existing, more empirical models. The model has crucial results for the conception of RO systems with high permeability membranes, as the reduction in membrane resistance in these systems conducts to a relative augmentation in the significance of CP in system efficiency [12].

7. Conclusion

The main points drawn from this study may be listed as below:

From the idea, which conducted to RO, where Samuel T. Yuster imagined the concept of utilizing the Gibb's adsorption equation as a road map to discover methods for making fresh water from brackish water and seawater, started a long history for a new revolutionary technology for desalination and water treatment.

Modeling RO technique still has great tasks to perform until a complete and exhaustive model will be obtained. Complicated and varying raw water qualities and quantities parameters through time and space are making hard to modelise perfectly this highly dynamic process. Facing to the increasing pollution

levels and trying to satisfy the drinking water guidelines, RO membrane modification is often required which made modeling RO process harder to accomplish.

In spite of its large success, RO remains a limited physical process which need more research in terms of design and construction to increase its performance.

List of Abbreviations

A	Solvent permeability coefficient
$\acute{a}$	Parameter in Eq. (9), dimensionless
$\acute{b}$	Parameter in Eq. (9), dimensionless
C_A	Solute concentration (mol m^{-3})
C_{Ai}	Molar concentration
C_{A1}	Feed bulk concentration
C_{A2}	Concentration of the boundary-film solution just outside the membrane on the high-pressure part
C_{A3}	Permeate concentration
CFD	Computational fluid dynamics
CP	Concentration polarization
D_{AB}	Solute diffusivity (m^2 s^{-1})
$D_{AB, ref}$	Reference solute diffusivity (m^2 s^{-1})
f	Separation (rejection or retention)
$\acute{f}$	Theoretical separation
F_j	Force
IT	Irreversible thermodynamics
J_i	Flux of component i through membrane, in Eq. (11)
k	Mass transfer coefficient for any solute (m/s)
k_{ref}	Mass transfer coefficient for a reference solute (m/s)
L_{ij}	Phenomenological coefficient
m_{A1}	Feed bulk molality (molal concentration)
m_{A3}	Permeate molality
N_A	Solute flux (kg m^{-2} s^{-1})
N_B	Solvent flux (kg m^{-2} s^{-1})
ORR	Onsager reciprocal relationship
PS-CF	Preferential sorption-capillary flow
R	Ideal gas constant (8.314 kg m^2 s^{-2} K^{-1} mol^{-1})
Re	Reynolds number, dimensionless
RO	Reverse osmosis
Sc	Shmidt number, dimensionless
Sh	Sherwood number, dimensionless
SD	Solution-diffusion (SD)
T	Temperature (K)
TDS	Total dissolved salts
TFC	Thin-film composite
UCLA	University of California at Los Angeles
v_B	Partial molar volume of the solvent (m^3 mol^{-1})
v_i	Partial molar volume of componemt i (m^3 mol^{-1})
v^+	Number of kmol of cations from dissociation of 1 kmol salt, dimensionless
v^-	Number of kmol of anions from dissociation of 1 kmol salt, dimensionless
X_B	Mole fraction of the solvent

Greek Symbols

ΔP	Applied pressure difference, from one side to the other of the membrane (Pa)
$\Delta P - \Delta \pi$	Efficient pressure driving force (Pa)
$\Delta \pi$	Osmotic pressure difference, from one side to the other of the membrane (Pa)
π	Osmotic pressure of a solution (Pa)
π_2	Osmotic pressure of a solution at one side of the membrane (Pa)
π_3	Osmotic pressure of a solution at the other side of the membrane (Pa)
σ	Staverman (or reflection) coefficient

References

[1] S. A. Creber, T. R. R. Pintelon, D. A. W. Graf von der Schulenburg, J. S. Vrouwenvelder, M. C. M. van Loosdrecht, M. L. Johns, Magnetic resonance imaging and 3D simulation studies of biofilm accumulation and cleaning on reverse osmosis membranes, Food Bioprod. Process. 88 (2010) 401-408.

[2] M. Verhuelsdonk, T. Attenborough, O. Lex, T. Altmann, Design and optimization of seawater reverse osmosis desalination plants using special simulation software, Desalination 250 (2010) 729-733.

[3] G. Srivathsan, Modeling of fluid flow in spiral wound reverse osmosis membranes, PhD Thesis, University of Minnesota, 2013.

[4] S. M. S. Ghiu, Mass transfer of ionic species in direct and reverse osmosis processes, PhD Thesis, University of South Florida, 2003.

[5] H. Mehdizadeh, Modeling of transport phenomena in reverse osmosis membranes, PhD Thesis, McMaster University, Ontario, 1990.

[6] L. E. Applegate, Membrane separation processes, Chem. Eng., June 11, (1984) 64-89.

[7] S. Sourirajan, Reverse osmosis, Academic Press, New York, 1970.

[8] S. Sourirajan, Reverse osmosis and synthetic membranes: Theory-technology-engineering, National Research Council Canada, Ottawa, Canada, 1977.

[9] B. R. Min, Experimental and theoretical study of NaCl and Ca Cl$_2$ transport through cellulose acetate membranes using a reverse osmosis batch cell, PhD Thesis, State University of New York at Buffalo, 1983.

[10] Z. Hu, A. Antony, G. Leslie, P. Le-Clech, Real-time monitoring of scale formation in reverse osmosis using electrical impedance spectroscopy, J. Membr. Sci. 453 (2014) 320-327.

[11] C. Ba, Design of advanced reverse osmosis and nanofiltration membranes for water purification, PhD Thesis, University of Illinois at Urbana-Champaign, 2010.

[12] W. Rohlfs, G. P. Thiel, J. H. Lienhard V, Modeling reverse osmosis element design using superposition and an analogy to convective heat transfer, J. Membr. Sci. 512 (2016) 38-49.

[13] A. E. Anqi, N. Alkhamis, A. Oztekin, Numerical simulation of brackish water desalination by a reverse osmosis membrane, Desalination 369 (2015) 156-164.

[14] Y. Wang, W. He, H. Zhu, Computational fluid dynamics (CFD) based modelling of osmotic energy generation using pressure retarded osmosis (PRO), Desalination 389 (2016) 98-107.

[15] J. I. Marriott, Detailed modelling and optimal design of membrane separation systems, PhD Thesis, University College London, 2001.

[16] A. K. Gautam, T. J. Menkhaus, Performance evaluation and fouling analysis for reverse osmosis and nanofiltration membranes during processing of lignocellulosic biomass hydrolysate, J. Membr. Sci. 451 (2014) 252-265.

[17] S. Jamaly, N. N. Darwish, I. Ahmed, S. W. Hasan, A short review on reverse osmosis pretreatment technologies, Desalination 354 (2014) 30-38.

[18] K. Jamal, M. A. Khan, M. Kamil, Mathematical modeling of reverse osmosis systems, Desalination 160 (2004) 29-42.

[19] S. Sourirajan, Thirty years of membrane research – A few highlights, Proc. Int. Memb. Conf. 25th Anniv. Memb. Res. Canada, M. Malalyandi, O. Kutowy, F. Talbot (Eds.), Ottawa, September 24-26, 3-32 (1986).

[20] A. Shrivastava, S. Rosenberg, M. Peery, Energy efficiency breakdown of reverse osmosis and its implications on future innovation roadmap for desalination, Desalination 368 (2015) 181-192.

[21] Saltwater intrusion, https://en.wikipedia.org/wiki/Saltwater_intrusion (accessed on 22/06/2017).

[22] S. T. Yuster, S. Sourirajan, K. Bernstein, Sea water demineralization by the 'surface skimming' process, University of California (UCLA), Dept. of Engineering, Rept. 58-26, March, 1958.

[23] S. Loeb, The Loeb-Sourirajan Membrane: How it came about, in: Synthetic membranes, A. F. Turback (Ed.), vol. 1, ACS Symposium Series 153, Washington, 1981.

[24] E. J. Jr., Breton, Water and ion flow through imperfect osmotic membranes, Office of saline water, US Dept. of the Interior, Res. & Dev. Prog. Rept. 16, April, 1957.

[25] C. E. Reid, E. J. Breton, Water and ion flow across cellulosic membranes, J. Appl. Polym. Sci. 1 (1959) 133-143.

[26] S. Loeb, S. Sourirajan, Sea water demineralization by means of an osmotic membrane, Advan. Chem. Ser. 38 (1962) 117-132.

[27] A. Altaee, G. Zaragoza, H. R. van Tonningen, Comparison between Forward Osmosis-Reverse Osmosis and Reverse Osmosis processes for seawater desalination, Desalination 336 (2014) 50-57.

[28] V. Haluch, E. F. Zanoelo, C. J. L. Hermes, Experimental evaluation and semi-empirical modeling of a small-capacity reverse osmosis desalination unit, Chem. Eng. Res. Design 122 (2017) 243-253.

[29] J. S. Kim, J. Chen, H. E. Garcia, Modeling, control, and dynamic performance analysis of a reverse osmosis desalination plant integrated within hybrid energy systems, Energy 112 (2016) 52-66.

[30] J. Lin, Molecular dynamics simulation of osmosis, reverse osmosis and electro-osmosis in electrolyte solutions, PhD Thesis, University of Illinois at Chicago, 2000.

[31] J.-S. Choi, J.-T. Kim, Modeling of full-scale reverse osmosis desalination system: Influence of operational parameters, J. Ind. Eng. Chem. 21 (2015) 261-268.

[32] A. R. Bartman, Control and monitoring of reverse osmosis water desalination, PhD Thesis, University of California, Los Angeles, 2011.

[33] J. Garcia-Aleman, Mathematical modeling of the pressure-driven performance of McMaster pore-filled membranes, McMaster University, Ontario, 2002.

[34] M. Soltanieh, W. N. Gill, Review of reverse osmosis membranes and transport models, Chem. Eng. Commun. 12 (1981) 279-363.

[35] J. Heo, L. K. Boateng, J. R. V. Flora, H. Lee, N. Her, Y.-G. Park, Y. Yoon, Comparison of flux behavior and synthetic organic compound removal by forward osmosis and reverse osmosis membranes, J. Membr. Sci. 443 (2013) 69-82.

[36] A. Saengrung, Modeling of reverse osmosis plants using system identification and neural networks, Master Thesis, Florida Atlantic University, 2002.

[37] K. Kezia, J. Lee, W. Ogieglo, A. Hill, N. E. Benes, S. E. Kentish, The transport of hydronium and hydroxide ions through reverse osmosis membranes, J. Membr. Sci. 459 (2014) 197-206.

[38] T.-U. Kim, Transport of organic micropollutants through nanofiltration (NF) and reverse osmosis (RO) membranes: Mechanisms, modeling, and applications, University of Colorado at Boulder, 2006.

[39] L. K. Boateng, Multiscale modeling of water transport and the influence of water quality parameters on membrane processes, PhD Thesis, University of South Carolina, 2016.

[40] A. F. Corral, Alternative technologies for inland desalination, PhD Thesis, The University of Arizona, 2014.

[41] E. Mancha, Alternatives to piloting in brackish waters: Accuracy and precision of commercial reverse osmosis membrane design model projections, PhD Thesis, The University of Texas at El Paso, 2012.

[42] Y. Xiang, Understanding membrane fouling mechanisms through computational simulations, PhD Thesis, The George Washington University, 2016.

[43] F. Daniels, R. A. Alberty, Physical chemistry, 3rd Ed., John Wiley and Sons, Inc., New York, 1972.

[44] R. W. Stoughton, M. H. Lietzke, Calaculation of some thermodynamic properties of sea salt solutions at elevated temperatures from data on NaCl solutions, J. Chem. Eng. Data, 10 (1965) 254-260.

[45] R. C. Weast, CRC handbook of chemistry and physics, 56th Ed., CRC Press, 1975.

[46] A. J. Staverman, Recueil Trav. Chim. Pays-Bas, 70 (1951) 344-352.

[47] H. G. Burghoff, K. L. Lee, W. Pusch, Characterization of transport across cellulose acetate membranes in the presence of strong solute – membrane interactions, J. Appl. Polym. Sci. 25 (1980) 323-347.

[48] A. J. Staverman, Structure and function of membranes, J. Membr. Sci. 16 (1983) 7-20.

[49] R. Salcedo-Díaz, P. García-Algado, M. García-Rodríguez, J. Fernández-Sempere, F. Ruiz-Beviá, Visualization and modeling of the polarization layer in crossflow reverse osmosis in a slit-type channel, J. Membr. Sci. 456 (2014) 21-30.

[50] A. Jogdand, A. Chaudhuri, Modeling of concentration polarization and permeate flux variation in a roto-dynamic reverse osmosis filtration system, Desalination 375 (2015) 54-70.

[51] K. M. Sassi, I. M. Mujtaba, Simulation and optimization of full scale reverse osmosis desalination plant, 20th European Symposium on Computer Aided Process Engineering – ESCAPE20, S. Pierucci, G. B. Ferraris (Eds.), Elsevier B. V.,

2010.

[52] M. A. Al-Obaidi, I. M. Mujtaba, Steady state and dynamic modeling of spiral wound wastewater reverse osmosis process, Comput. Chem. Eng. 90 (2016) 278-299.

[53] R. B. Bird, W. E. Stewart, E. N. Lightfoot, Transport phenomena, John Wiley and Sons, Inc., New York, 1960.

[54] J. L. Siler, Reverse osmosis membranes concentration polarization and surface fouling: Predictive models and experimental verifications, PhD Thesis, The University of Kentucky, 1987.

[55] G. Srivathsan, E. M. Sparrow, J. M. Gorman, Reverse osmosis issues relating to pressure drop, mass transfer, turbulence, and unsteadiness, Desalination 341 (2014) 83-86.

[56] W. Lawler, J. Alvarez-Gaitan, G. Leslie, P. Le-Clech, Comparative life cycle assessment of end-of-life options for reverse osmosis membranes, Desalination 357 (2015) 45-54.

[57] R. E. Kesting, Synthetic polymeric membranes: A structural perspective, 2nd Ed., John Wiley and Sons, New York, 1985.

[58] T. Fujioka, N. Oshima, R. Suzuki, W. E. Price, L. D. Nghiem, Probing the internal structure of reverse osmosis membranes by positron annihilation spectroscopy: Gaining more insight into the transport of water and small solutes, J. Membr. Sci. 486 (2015) 106-118.

[59] T. Fujioka, S. J. Khan, J. A. McDonald, A. Roux, Y. Poussade, J. E. Drewes, L. D. Nghiem, Modelling the rejection of N-nitrosamines by a spiral-wound reverse osmosis system: Mathematical model development and validation, J. Membr. Sci. 454 (2014) 212-219.

[60] J. Duan, E. Litwiller, I. Pinnau, Preparation and water desalination properties of POSS-polyamide nanocomposite reverse osmosis membranes, J. Membr. Sci. 473 (2015) 157-164.

[61] N. Y. Yip, Sustainable production of water and energy with osmotically-driven membrane processes and ion-exchange membrane processes, PhD Thesis, Yale University, 2014.

[62] B. M. Carter, Design, development, and evaluation of thin-film composite bicontinuous cubic lyotropic liquid crystal polymer membranes for water filtration applications, PhD Thesis, University of Colorado, 2014.

[63] J. E. Cadotte, R. J. Peterson, Thin-film composite reverse-osmosis membranes: Origin, development, and recent advances, in: Synthetic membranes, A. F. Turbak (Ed.), vol. 1, ACS Symposium Series, Washington, 1980.

[64] A. M. Kamal, T. A. El-Sayed, A. M. A. El-Butch, S. H. Farghaly, Analytical and finite element modeling of pressure vessels for seawater reverse osmosis desalination plants, Desalination 397 (2016) 126-139.

[65] W. He, Y. Wang, A. Sharif, M. H. Shaheed, Thermodynamic analysis of a stand-alone reverse osmosis desalination system powered by pressure retarded osmosis, Desalination 352 (2014) 27-37.

[66] J. E. Cadotte, R. J. Petersen, R. E. Larson, E. E. Erickson, A new thin-film composite sea water reverse osmosis membrane, Desalination 32 (1980) 25-31.

[67] R. E. Larson, J. E. Cadotte, R. J. Petersen, The FT-30 seawater reverse osmosis membrane: Element test results, Desalination 38 (1981) 473-483.

[68] R. E. Larson, R. J. Petersen, P. K. Eriksson, Test results on FT-30 eight-inch-diameter seawater and brackish water reverse osmosis elements, Desalination 46 (1983) 81-90.

[69] J. E. Cadotte, Evolution of composite reverse osmosis membranes, in: Material Science of Synthetic Membranes, D. R. Lloyd (Ed.), ACS Symposium Series 269, Washington, 1985.

[70] M. A. Al-Obaidi, C. Kara-Zaïtri, I. M. Mujtaba, Removal of phenol from wastewater using spiral-wound reverse osmosis process: Model development based on experiment and simulation, J. Water Process Eng. 18 (2017) 20-28.

[71] M. A. Al-Obaidi, C. Kara-Zaitri, I. M. Mujtaba, Scope and limitations of the irreversible thermodynamics and the solution diffusion models for the separation of binary and multi-component systems in reverse osmosis process, Comput. Chem. Eng. 100 (2017) 48-79.

[72] M. A. Al-Obaidi, J-P. Li, C. Kara-Zaïtri, I. M. Mujtaba, Optimisation of reverse osmosis based wastewater treatment system for the removal of chlorophenol using genetic algorithms, Chem. Eng. J. 316 (2017) 91-100.

[73] G. Belfort, Membrane modules: Comparison of different configurations using fluid mechanics, J. Membr. Sci. 35 (1988) 245-270.

[74] J. S. Vrouwenvelder, C. Picioreanu, J. C. Kruithof, M. C. M. van Loosdrecht, Biofouling in spiral wound membrane systems: Three-dimensional CFD model based evaluation of experimental data, J. Membr. Sci. 346 (2010) 71-85.

[75] A. I. Radu, L. Bergwerff, M. C. M. van Loosdrecht, C. Picioreanu, A two-dimensional mechanistic model for scaling in spiral wound membrane systems, Chem. Eng. J. 241 (2014) 77-91.

[76] A. I. Radu, J. S. Vrouwenvelder, M. C. M. van Loosdrecht, C. Picioreanu, Modeling the effect of biofilm formation on reverse osmosis performance: Flux, feed channel pressure drop and solute passage, J. Membr. Sci. 365 (2010) 1-15.

[77] C. Picioreanu, J. S. Vrouwenvelder, M. C. M. van Loosdrecht, Three-dimensional modeling of biofouling and fluid dynamics in feed spacer channels of membrane devices, J. Membr. Sci. 345 (2009) 340-354.

[78] J. M. Dickson, Fundamental aspects of reverse osmosis, in: Reverse osmosis technology: Application for high-purity-water production, B. S. Parekh (Ed.), Marcel Dekker, Inc., New York, 1988.

[79] O. Kedem, A. Katchalsky, Thermodynamic analysis of the permeabilty of biological membranes to non- electrolytes, Biochem. Biophys. Acta 27 (1958) 229-246.

[80] K. S. Spiegler, O. Kedem, Thermodynamics of hyperfiltration (reverse osmosis): Criteria for efficient membranes, Desalination 1 (1966) 311-326.

[81] V. Sasidhar, Role of electrokinetic phenomena and of transport facilitation in membrane processes, PhD Thesis, State University of New York at Buffalo 1983.

[82] W. Banks, A. Sharples, Studies on desalination by reverse osmosis: III. Mechanism of solute rejection, J. Appl. Chem. 16 (1966) 153-158.

[83] H. K. Lonsdale, U. Merten, R. L. Riley, Transport properties of cellulose acetate osmotic membranes, J. Appl. Polym. Sci. 9 (1965) 1341-1362.

[84] K. Kezia, J. Lee, A. J. Hill, S. E. Kentish, Convective transport of boron through a brackish water reverse osmosis membrane, J. Membr. Sci. 445 (2013) 160-169.

[85] T. K. Sherwood, P. L. T. Brian, R. E. Fisher, Desalination by reverse osmosis, 1&EC Fund 6 (1967) 2-12.

[86] E. Glueckauf, On the mechanism of osmotic desalting with porous membranes, Proc. First Int. Symp. on water desalination, Washington, US Dept. Interior, Office of Saline Water, 1 (1965) 143-156.

[87] E. Glueckauf, The distribution of electrolytes between cellulose acetate membrane and aqueous solutions, Desalination 18 (1976) 155-172.

[88] L. Onsager, Reciprocal relations in irreversible processes, Phys. Rev. 37 (1931) 405-425.

[89] P. Xie, L. C. Murdoch, D. A. Ladner, Hydrodynamics of sinusoidal spacers for improved reverse osmosis performance, J. Membr. Sci. 453 (2014) 92-99.

[90] P. Xie, Simulation of reverse osmosis and osmotically driven membrane processes, PhD Thesis, Clemson University, 2016.

[91] L. Song, S. Yu, Concentration polarization in cross-flow reverse osmosis, AIChE J. 45 (1999) 921-928.

[92] W. W. Focke, P. G. J. M. Nuijens, Velocity profile caused by a high porosity spacer between parallel plates (membranes), Desalination 49 (1984) 243-253.

[93] S. Karode, A. Kumar, Flow visualization through spacer filled channels by computational fluid dynamics I. Pressure drop and shear rate calculations for flat sheet geometry, J. Membr. Sci. 193 (2001) 69-84.

[94] M. Shakaib, S. M. F. Hasani, M. Mahmood, CFD modeling for flow and mass transfer in spacer-obstructed membrane feed channels, J. Membr. Sci. 326 (2009) 270-284.

[95] A. Subramani, S. Kim, E. M. V. Hoek, Pressure, flow, and concentration profiles in open and spacer-filled membrane channels, J. Membr. Sci. 277 (2006) 7-17.

[96] K. Madireddi, A transient model for predicting concentration polarization in commercial spiral wound membranes, PhD Thesis, University of California, Los Angeles, 1996.

[97] M. F. Gruber, U. Aslak, C. Hélix-Nielsen, Open-source CFD model for optimization of forward osmosis and reverse osmosis membrane modules, Sep. Purif. Technol. 158 (2016) 183-192.

[98] M. Park, J. Lee, C. Boo, S. Hong, S. A. Snyder, J. H. Kim, Modeling of colloidal fouling in forward osmosis membrane: Effects of reverse draw solution permeation, Desalination 314 (2013) 115-123.

[99] S. Kim, E. M. V. Hoek, Modeling concentration polarization in reverse osmosis processes, Desalination 186 (2005) 111-128.

[100] H. Yuan, I. M. Abu-Reesh, Z. He, Mathematical modeling assisted investigation of forward osmosis as pretreatment for microbial desalination cells to achieve continuous water desalination and wastewater treatment, J. Membr. Sci. 502 (2016) 116-123.

[101] T.-U. Kim, J. E. Drewes, R. S. Summers, G. L. Amy, Solute transport model for trace organic neutral and charged compounds through nanofiltration and reverse osmosis membranes, Water Res. 41 (2007) 3977-3988.

[102] S. S Manickam, J. R. McCutcheon, Model thin film composite membranes for forward osmosis: Demonstrating the inaccuracy of existing structural parameter models, J. Membr. Sci. 483 (2015) 70-74.

[103] D. Ghernaout, A. El-Wakil, Requiring reverse osmosis membranes modifications – An overview, Am. J. Chem. Eng. 5 (2017) 81-88.