

Membrane-based Desalination Technologies: Analysis and Analogy to Heat Exchangers

BY

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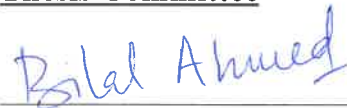
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DEDICATION

To my beloved family and dedicated advisor,
Your continuous support and guidance have been the first motive
of my journey. I am deeply grateful to you all.

With heartfelt appreciation,

Omar A. Alrafee

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NOMENCLATURE

Abbreviations

NF	:	Nanofiltration
RO	:	Reverse Osmosis
ED	:	Electrodialysis
NTU	:	number of transfer units
MTU	:	mass transfer units
IT	:	Irreversible Thermodynamics Model
SDM	:	Solution-Diffusion Model
SC	:	Space-Charge Model
TMS	:	Teorrell–Meyer–Sievers Model
NDP	:	Net Driving Pressure
CEM	:	Cation Exchange Membranes
AEM	:	Anion Exchange Membranes
RR	:	Recovery Ratio
TR	:	Transport Ratio
CR	:	Concentration Ratio
ER	:	Resistance Ratio
CF	:	Concentration Factor
SR	:	Osmotic Pressure Ratio
ST_s	:	Salt Transport Ratio
SP	:	Salt Passage
S_{rej}	:	Salt Rejection

Symbols

U	:	Electrical Potential Difference (V)
U_{th}	:	Overall Heat Transfer Coefficient (W/m^2K)
$\dot{Q}_{th}$	:	Thermal Flow Rate (W)
$\dot{Q}$	:	Volume Flow Rate (m^3/s)
$\dot{m}$	:	Mass Flow Rate (kg/s)

i	:	Current Density (A/m^2)
i_{lim}	:	limiting current density
i_v	:	Van 'T Hoff Factor
c	:	Molarity of the Solution (mol/m^3)
b	:	Molarity of the Solution (mol/kg)
R	:	Ideal Gas Constant ($kJ/mol\ K$)
T	:	Absolute Temperature (K)
w	:	Salt Concentration (g/kg)
ρ	:	Density (kg/m^3)
C	:	Modified Van't Hoff Coefficient ($kPa\ kg/g$)
K_w	:	Water Permeability Coefficient ($m^3/m^2\cdot s\cdot kPa$)
K_s	:	Permeability Coefficient of Salt ($m^3/m^2\cdot s$)
P	:	Hydraulic Pressure (kPa)
A_w	:	Modified Water Permeability Coefficient
A_m	:	Membrane Surface Area
A_{prac}	:	Practical Area (m^2)
A_{eff}	:	Effective Surface Area (m^2)
c_s	:	Salt Concentration (g/s)
T_s	:	Salt Transport Rate (mol/s)
C_s^Δ	:	Amount Of Salinity (mol/m^3)
C_x	:	Salinity of the water in a stream (mol/m^3)
z	:	Valence
F	:	Faraday constant ($A\ s/mol$)
r	:	Resistance (Ωm^2)
s	:	Safety Factor
u	:	Linear Velocity (Intrinsically Averaged Velocity) (m/s)
L_{prac}	:	Practice Length (m)
L_{st}	:	Length of a Stack (m)
w	:	Effective Width of Cell (m)

N_{cp}	:	Number Of Cell Pairs
N_{st}	:	Total Number of Stacks

Subscripts

f	:	Feed
p	:	Permeate
c	:	Concentrate
d	:	Dilute
s	:	Salt
w	:	Water
cp	:	Cell Pair
st	:	Stack
tot	:	Total
m	:	Membrane
don	:	Donnan Potential
eff	:	Effective
$prac$	:	Practical
hrd	:	Hybrid

Greek Symbols

ε	:	The Effectiveness
π	:	Osmotic Pressure (kPa)
ϕ	:	Osmotic Coefficient
λ_o	:	Permeability-Feed Osmotic Pressure Ratio
Δ	:	Compartment (Channel) Thickness (m)
ζ	:	Current Utilization Factor
β	:	Shadow Factor
κ_{av}	:	Specific Electrical Conductivity (S/m)
κ	:	Electrical Conductivities (S/m)
Λ	:	Equivalent Conductance (Sm^2/keq)
δ	:	Boundary Film Thickness (m)

ABSTRACT

Full Name : Omar Abdullah Alrafee
Thesis Title : Membrane-based Desalination Technologies: Analysis and Analogy to Heat Exchangers
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The need for water in the world increases daily due to factors such as population growth, industrial water demands and climate change. Therefore, researchers and industries have focused on water desalination and related technologies. Before, reliance was placed on thermal desalination methods but, after the development of membrane desalination technologies, it has become a pioneering method and has outperformed thermal desalination in efficiency and sustainability. Nanofiltration (NF) is a prominent pressure-based membrane desalination technology, representing an advanced method for treating water sources of different salinities. Electrolysis (ED) is a membrane desalination technology that uses ion extraction under the influence of an electric field to treat brackish water effectively. Integrating these desalination techniques with each other or Reverse Osmosis (RO) into different hybrid systems optimizes ion removal and system efficiency.

A dimensionless design model for NF and ED is developed by using the Mass Transfer Units (MTU) concept. MTU is analogous to the Number of Transfer Units (NTU) concept used in rating and sizing heat exchangers. This analogy aims to quantify the transfer of materials across the membranes of each technology. For NF, permeate water is the main focus while salt transport is the analysed parameter in the ED model. The aim of this thesis is to relate the MTU to the extent of the success of transporting the materials across the membranes i.e. its effectiveness (ϵ). Using the effectiveness, it enables engineers to take the necessary decisions to improve the designed system. The development of the ϵ -MTU model is also extended to hybrid systems that combined membrane desalination technologies such as RO, NF and ED.

For NF, a linear function of salinity was used to define the osmotic pressures in reaching the closed-form solutions which determine the performance for the mass exchanger. The model relates membrane and NF characteristics such as size, pressures and salinities to recovery ratio and the effectiveness. The effectiveness of an NF system is defined as the recovery ratio divided by its maximum achievable value. The model can also reproduce the results of a RO system by assuming 100% salt rejection. It is validated by comparison with data in the literature for four NF plant designs, yielding errors ranging from 0.73% to 5.42%, with an average error of 3.9%. Same concept is applied for ED mass exchangers, where its effectiveness is defined as the system transport ratio over its maximum possible value. Two different modelling results are shown depending on whether the ED system is dealing with brackish water or a high salinity source. The modelling errors found are ~ 0.02 % for the brackish water source (3500 ppm) and ~ 2 % for the high salinity source (150,000 ppm). Therefore, the ϵ -MTU model developed can help to design and evaluate ED systems in a robust manner. These modelling concepts were also applied to the above-mentioned hybrid systems which allowed for a comprehensive analysis of the integrated system, considering both chemical and hydraulic aspects.

ملخص الرسالة

الاسم الكامل: عمر عبدالله الريفي

عنوان الرسالة: تقنيات تحلية المياه القائمة على الأغشية: التحليل والمقارنة للمبادلات الحرارية

التخصص: الهندسة الميكانيكية

تاريخ الدرجة العلمية: ديسمبر ٢٠٢٣

تتزايد حاجة العالم للمياه يوماً بعد يوم بسبب عوامل مثل نمو السكان واحتياجات الصناعة للمياه وتغير المناخ. لذلك، ركز الباحثون والصناعات على تقنيات تحلية المياه والتقنيات ذات الصلة. في السابق، كان يعتمد على طرق التحلية الحرارية ولكن بعد تطوير تقنيات التحلية بالأغشية، أصبحت وسيلة رائدة وتوفرت على التحلية الحرارية من حيث الكفاءة والاستدامة. تعد الترشيح النانوي (NF) تقنية تحلية بالأغشية تعتمد على الضغط بارزة، وتمثل طريقة متقدمة لمعالجة مصادر المياه ذات الملوحة المختلفة. التحلية الكهربائية (ED) تقنية تحلية بالأغشية تستخدم استخراج الأيونات تحت تأثير الحقل الكهربائي لمعالجة المياه المالحة بفعالية. يمكن دمج هذه التقنيات للتحلية مع بعضها البعض أو مع التناضح العكسي (RO) في أنظمة هجينة مختلفة لتحسين إزالة الأيونات وكفاءة النظام.

تم تطوير نموذج تصميم بُعد لـ NF و ED باستخدام مفهوم وحدات نقل الكتلة (MTU). تشبه MTU المفهوم المعروف باسم عدد وحدات النقل (NTU) المستخدم في تقييم وتحجيم مبادلات الحرارة. تهدف هذه التشابهية إلى كمية نقل المواد عبر أغشية كل تقنية. بالنسبة لـ NF، يكون ماء النفاذ هو التركيز الرئيسي بينما يتم تحليل نقل الملح في نموذج ED. الهدف من هذه الأطروحة هو ربط MTU بمدى نجاح نقل المواد عبر الأغشية أي فعاليته (ϵ). باستخدام الفعالية، يُمكن للمهندسين اتخاذ القرارات اللازمة لتحسين النظام المصمم. كما يتم توسيع تطوير نموذج ϵ -MTU إلى الأنظمة الهجينة التي تجمع بين تقنيات تحلية الأغشية مثل RO و NF و ED.

لتحديد الضغوط الاسموزية التي تحقق الحلول بصورة مغلقة والتي تحدد الأداء لتبادل الكتلة، تم استخدام وظيفة خطية للملوحة في حالة NF. يرتبط النموذج بالخصائص الغشائية و NF مثل الحجم والضغط والملوحات بنسبة الاسترجاع والفعالية. تُعرف فعالية نظام NF بأنها نسبة الاسترجاع مقسومة على قيمتها القصوى الممكنة. يمكن للنموذج أيضاً إعادة إنتاج نتائج نظام RO عن طريق افتراض رفض الملح بنسبة 100%. يتم التحقق من صحة النموذج من خلال المقارنة مع البيانات في الأدب لأربعة تصاميم محطات NF، مما يؤدي إلى أخطاء تتراوح بين 0.73% و 5.42%، مع متوسط خطأ قدره 3.9%. يتم تطبيق نفس المفهوم لمبادلات الكتلة ED، حيث تُعرف فعاليته كنسبة نقل النظام على قيمتها القصوى الممكنة. يُعرض نتيجتنا نمذجة مختلفان اعتماداً على ما إذا كان النظام ED يتعامل مع مياه مالحة أو مصدر ذو ملوحة عالية. الأخطاء في النمذجة تتراوح حوالي 0.02% لمصدر المياه المالحة (3500 جزء في المليون) وحوالي 2% لمصدر الملوحة العالية (150,000 جزء في المليون). لذلك، يمكن لنموذج ϵ -MTU المطور المساعدة في تصميم وتقييم أنظمة ED بطريقة قوية. تم تطبيق هذه المفاهيم النمذجية أيضاً على الأنظمة الهجينة المذكورة أعلاه مما سمح بتحليل شامل للنظام المتكامل، مع مراعاة الجوانب الكيميائية والهيدروليكية على حد سواء.

Chapter 1

Introduction

{We have made from water every living thing} (30, Al-Anbiya)

1.1. Aquatic Dilemma

Water connects every aspect of life. It covers most of our planet. But it's rare to have freshwater. The water crisis is one of the most important issues in the last decades. Around 1.2 billion people around the world don't have much access to water [2]. Also, 2.7 billion people face water scarce for at least one month yearly. Moreover, 2.4 billion people have Inadequate sanitation issues that might lead them be exposed to water-borne or fatal diseases [3] Hence, scientists, researchers, and engineers are exploring diverse avenues to deliver water solutions that are highly productive while ensuring a maximally effective approach.

1.2. Desalination: A Key Pillar in Water Crisis Solutions

To manage and solve freshwater scarcity, desalination technologies are taken as a practical solution these days. There are two common kinds of desalination, which are Thermal-based desalination, such as humidification dehumidification and multi-effect desalination and membrane desalination, and membrane-based desalination such as reverse osmosis (RO), Nanofiltration (NF), and electrodialysis (ED) [4]. To achieve the product water in thermal desalination systems, high energy is consumed during the treatment of the feed that gives the dilute and drain the left

concentrated solution as brine. On the other hand, membrane processes utilize membrane film as a physical barrier to conduct the separation without phase change [5].

For the last two decades, membrane desalinations have been covering most of the desalination plants since it has high effectiveness, it doesn't require high energy consumption, and it requires lower cost. For saline water that is in the order of seawater, RO and NF are very efficient technologies in consuming energy. On the other side, in order to decrease the concentration of high-salinity sources to the level of the seawater, electrodialysis is in this case more efficient and productive. ED also has less fouling and scaling compared to RO and NF [6–8]. Nanofiltration is a membrane filtration-based method that has properties in between ultrafiltration (UF) and reverse osmosis (RO). Its function is to separate the molecules that are dissolved in an organic solution using the pressure as a driving force. The molecules separation depends on their shape, size, and charge [9].

For over 60 years, ED and NF have been becoming interest fields in a lot of research and industrial applications. Their models and applications have been so widely examined and mathematically simulated to produce significant developments [9], [10]. One of the methods that can be used for describing the performance of ED or NF systems is by developing an analogy to a similar system. The heat exchanger system shows an operation similarity that can be analyzed between it and ED/NF systems. This analogy can help in designing and evaluating systems performance.

1.3. Heat Exchangers and Mass exchangers

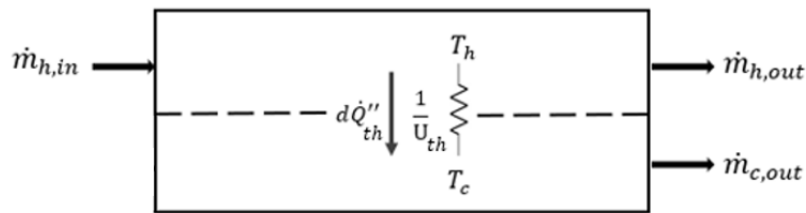


Figure 1-1(a). Schematic drawings of Heat exchanger with one inlet streams

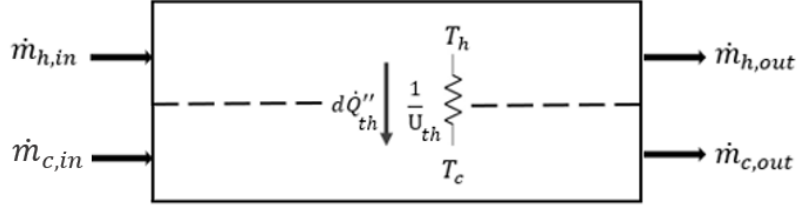


Figure 1-1(b). Schematic drawings of Heat exchanger with two inlet streams

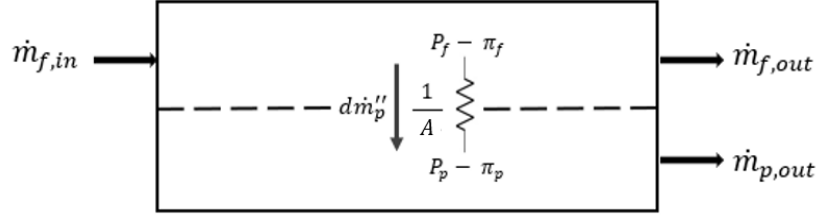


Figure 1-1(c). Schematic drawings of NF mass exchanger with two inlet streams

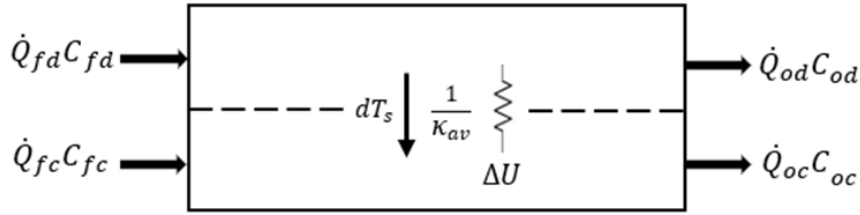


Figure 1-1(d). Schematic drawings of ED mass exchanger with two inlet streams

1.3.1. Nanofiltration, the linearity of osmotic pressure

For NF mass exchangers, a pressure driving force is applied for the separation process of salt between two compartments that are separated by a membrane. The osmotic pressure within a stream fluctuates in relation to the concentration of dissolved salts present in the water. The analytical modelling requires an assumed linear relationship between osmotic pressure and salinity. Though, while this assumption is valid for low-salinity solutions, it deviates from linearity when dealing with more saline waters.

The van 't Hoff equation for osmotic pressure is a mathematical expression that relates osmotic pressure to the concentration of solute particles in a solution. It is represented as [11].

$$\pi = i_v RTc \quad (1.1)$$

where i_v is the van 't Hoff factor (the number of particles formed when a solute dissolves), c is the molarity of the solution (mol/m^3), R is the ideal gas constant, T is the absolute temperature. Since the molarity is a function of salinity, the density of solution, and the molecular weight of solute, it can be expressed as the following [12]:

$$c = \frac{\rho_{solution} w}{M_{solute}} \quad (1.2)$$

where w is the concentration of the solute. Van't Hoff equation is assumed for low salinity solutions, so the density can be approximated to be same as pure water density (i.e. $\rho_{solution} \approx \rho_{pure}$). Substituting Eq. (1.1) to Eq. (1.2) gives an expression that can be used to define a modified van't Hoff coefficient, C , as a coefficient for linearizing the osmotic pressure function [12].

$$\pi = \frac{i_v R T \rho_{pure}}{M_{solute}} w = C w \quad (1.3)$$

Fig. 1-2 shows the relationship between the salinity in (g/kg) and the osmotic pressure caused by this solution salinity. The graph indicates that the relationship between salinity and osmotic pressure remains linear from 0 g/kg to 120 g/kg. Beyond this range, the correlation deviates from linearity and takes on a nonlinear pattern. This proves that the equation of the modified Van't Hoff factor can be used as long as the solution's salinity is maintained within the specified range from 0 g/kg to 120 g/kg.

To determine the value of C , the linear relationship is segmented into three intervals: 0-35 g/kg, 35-70 g/kg, and 70-120 g/kg. For each interval, a straight-line equation is employed, and the slope of these lines indicated the value of C . See Table 1-1 for resulted values.

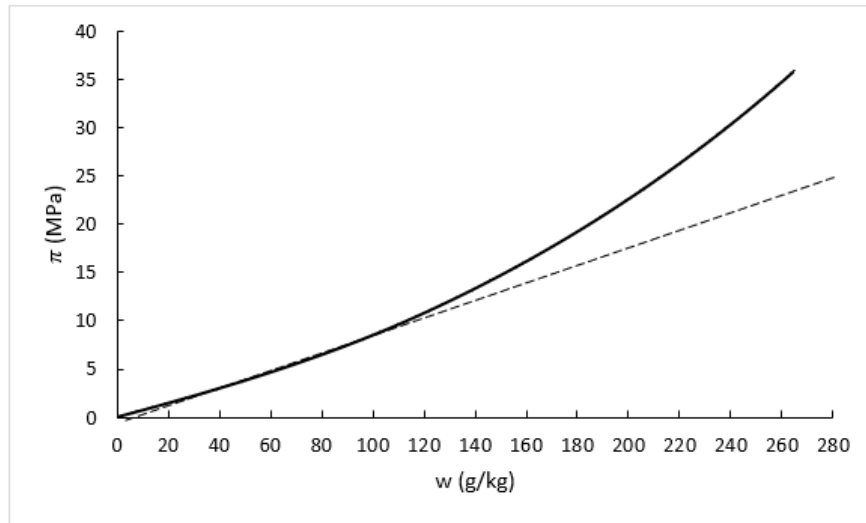


Figure 1-2. Osmotic pressures vs salinity at $T = 25^\circ\text{C}$.

Table 1-1. Modified van 't Hoff coefficients for three ranges of salinity.

w (g/kg)	C (kPa kg/g)
0 – 35	73.45
35 – 70	76.76
70 – 120	82.65

1.3.2. The effectiveness-number of transfer units model

Effectiveness-NTU methods are used widely in designing heat exchangers and evaluating its performance [13]. NTU is a one dimensionless parameter that combines several parameters, which are transfer area, the overall heat transfer coefficients, heat capacity, and fluid flow rate. With these dimensionless correlations, NTU can be used to estimate geometric and design parameters. Many efforts have been made over the last decade to build dimensionless correlations between performance and the number of transfer units for both heat and mass transfer.

1.3.3. The effectiveness-mass transfer units model

A strong analogy can be found between heat exchanger and nanofiltration desalination technology (Osmotic Mass Exchanger) and electrodialysis desalination system (Electric Mass Exchanger). A similar method of ε -NTU can be developed for designing NF and ED that can be indicated as ε -MTU. This method is used to relate some membranes and NF (such as the size, applied pressure, recovery ratio, etc.) and ED parameter (such as the size, total applied potential, salt transport, etc.) to the recovery ratio, salt transport, and the effectiveness that are defined for the model of the mass exchangers. The governing equations for mass exchangers are nondimensionalized under convenient assumptions by using some defined dimensionless groups combining their parameters. The model helps in sizing and evaluating the performance of the systems. The analogy can also be used for hybrid systems that combine different mass exchangers. This helps us understand how efficiently these systems, involving multiple mass exchange processes, perform as a unified unit.

Using ε -NTU method comes with inherent limitations and assumptions that help in simplifying the analysis such as steady-state operation, uniform fluid properties, and neglect of factors like axial heat conduction and phase change phenomena. Additionally, for using the effectiveness Mass Transfer Unit (ε -MTU) method in analyzing mass exchangers, there are also limitations and assumptions that need consideration:

Membrane Selectivity Assumption: Assumes ideal solute separation based on size and charge, potentially oversimplifying actual membrane performance.

No Fouling or Scaling: Neglects potential fouling and scaling effects, which can reduce permeate flux and efficiency over time.

Constant Operating Conditions: Assumes steady conditions, ignoring variations that may occur during operation.

Ideal Solution Behavior: Solutes in a solution behave perfectly according to idealized thermodynamic principles. In an ideal solution, solute-solvent interactions are assumed to be negligible, and the solution's properties (such as concentration, density, and viscosity) follow simple mathematical relationships.

Salt transport direction: Assuming salt transfer occurs primarily perpendicular to the membrane's surface.

Chapter 2

Analogy of Nanofiltration Mass Exchanger to Heat Exchanger

Chapter Abstract:

Heat and mass transfer processes have long been known to be analogous. Based upon this, it is understood that heat exchangers and nanofiltration (NF) systems share a strong analogy. A method similar to ϵ -NTU is developed for designing NF mass exchangers that can be called ϵ -MTU (effectiveness-mass transfer units). This method is used to relate membrane and NF parameters (such as the size, pressures, salinities, etc) to the recovery ratio and system effectiveness resulting in a closed form solution. The governing equations are non-dimensionalized based upon reasonable assumptions such as the linear relation between osmotic pressure and salinity. The effectiveness of a NF system is defined as the recovery ratio over its maximum possible value. It was also found that results for a RO system may be replicated assuming 100% salt rejection. The solution is tested by comparing data contained in the literature for four NF plant designs. The errors range from 0.73% to 5.42% while the average error was 3.9%. This ϵ -MTU model developed is more general and can help to design and evaluate NF as well as RO systems.

2.1. Introduction

Nanofiltration (NF) is a membrane separation technology that is used to soften and disinfect water by removing divalent and trivalent ions using membranes of a pore size range of 0.2-2 nm [14]. The hydraulic pressure acts as a driving force that is used to overcome the osmotic pressure of the feed solution. During a NF process, the feed water is forced through the membrane under pressure, and dissolved particles as well as contaminants are kept on the surface of the membrane. The pore size of the membrane provides high rejection of multivalent ions and small uncharged solutes, which make the residual feed stream to be more concentrated and collected as a brine. Diluted water that is diffused to the lower pressure permeate side is collected as the system product.

There are many mathematical transport models for NF mixed-ion systems that are commonly used to predict their behavior and to optimize performance. NF modelling can be done with or without considering the transport mechanism [15]. The irreversible thermodynamics (IT) model is a mechanism-independent model that was derived by Kedem and Katchalsky [16], and Spiegler and Kedem [17]. Considering specific assumptions in the IT model, a simpler approach is the so-called Solution-Diffusion model (SDM), which was introduced by Lonsdale [18]. It treats the membrane as a black box that ignores the transport mechanism by neglecting the porosity of the membrane. The fluxes of the water and solution depend on the operating and osmotic pressures, which are considered to be the driving forces of the system. Many research studies were conducted to develop SDM and enhance its accuracy since it does not include the effects of membrane transport mechanisms [6–9]. Some of the studies focused on the operational effects of fouling and concentration polarization on the membrane [10–12]. The rejection of electrolytes using a charged NF membrane is also further explained by Murthy and Chaudhari [13–14], using Spiegler–Kedem IT model equations.

Other mechanistic models were developed to investigate the membrane structure as well as its physical and chemical characteristics [15]. These mechanistic models are categorised as space-

charge (SC) [15–18] and Teorrell–Meyer–Sievers (TMS) models [19–20]. The SC model was further developed by Smit and co-workers [21–22] and Yaroshchuk and co-workers [23–26]. However, the SC model shows mathematical complexity and has high computational costs. TMS is a mechanistic model that is less complex compared to SC model. It is based on the assumption of a uniform distribution of fixed charges and mobile species, which make it more applicable [27–28]. More detailed and extensive work was done by Bowen and co-workers [28–31] and Kimura and co-workers [27, 32–35]. These models consider many physical and physicochemical characteristics of the membrane.

In heat exchangers, there are two paths for fluid flow with different temperatures as shown in Fig. 2-1(a). This figure shows a phase change heat exchanger, which has a hot fluid with varying temperature and a constant-temperature cold fluid. The differential heat transfer ($d\dot{Q}''$) is a result of the temperature difference between the hot and cold fluids. The reciprocal of the overall heat transfer coefficient (U) represents the resistance to the heat flow per unit area. A similar schematic drawing is made for the mass exchanging NF system which is analogous to this heat exchanger (See Fig. 2-1(b)). The feed with high concentration, hydraulic pressure, and osmotic pressure enters at the inlet of the mass exchanger. Some of the fluid is forced through the semipermeable membrane that rejects divalent ions and larger monovalent ions such as heavy metals. The rest of the feed leaves the mass exchange from the feed outlet with higher salinity. The permeate is accumulated as diluted fluid, and the concentrated fluid is accumulated as brine. Net driving pressure (NDP) is the difference of the hydraulic and osmotic pressures between both sides. NDP is the driving force of the mass exchanger that forces the transport of diluted water from the feed stream to the permeate stream. The reciprocal of the permeability coefficient of water (K_w) represents the resistance to mass transfer per unit area.

The effectiveness-number of transfer units (ϵ -NTU) method, developed by Kays and London [48], is used in heat exchanger design. It also helps in evaluating the performance of the heat exchanger

[49]. This method has the effectiveness, the number of transfer units (NTU), and the heat capacity rate ratio as three groups that are dimensionless. The effectiveness is the ratio of the actual heat transferred to the maximum possible heat transfer. The NTU combines multiple parameters, which are heat transfer area, the overall heat transfer coefficient, specific heat capacity and fluid flow rate. The heat capacity rate ratio is the ratio of minimum to the maximum stream thermal capacitances. Many efforts have been made over the last few decades to build dimensionless

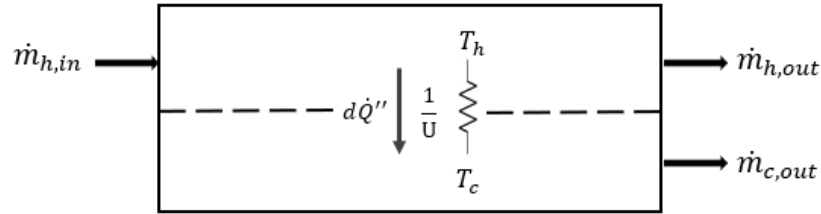


Fig. 2-1(a). Schematic drawing of heat exchanger with single inlet stream

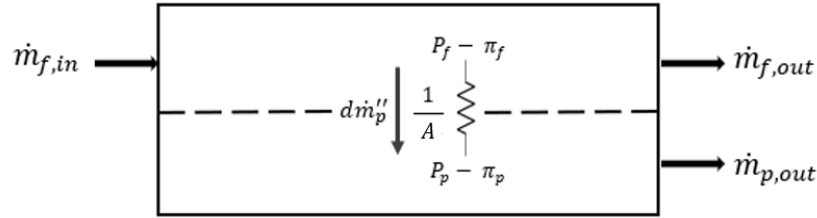


Fig. 2-1(b). Schematic drawing of NF mass exchanger with single inlet stream

correlations between performance and the number of transfer units for both heat and mass transfer. With these dimensionless correlations, ε -NTU can be used to estimate geometric and design parameters.

In this paper, a series of analytical equations are derived to develop an ε -MTU (effectiveness-mass transfer units) method for NF mass exchangers. Some parameters are defined and used to obtain the dimensionless differential permeate flow rate equation that is solved to give a closed form expression. This expression helps in connecting the input condition of the operation to the effective size and performance of the NF system. A number of plots are drawn for the obtained non-dimensional form, and the ε -MTU method is tested on a number of NF plants to validate the work and to show the use of the method in designing NF systems.

2.2. Nanofiltration mass exchanger model

A high salinity feed enters a channel to flow alongside the semi-permeable membrane as shown in Fig. 2-2 that represents the NF mass exchanger. The feed solution has the inlet conditions, which are the mass flow rate, high hydraulic pressure, and the osmotic pressure due to its salinity. A portion of the feed transports through the semi-permeable membrane to the permeate side as the feed is flowing throughout the length of the exchanger, leaving the remaining to have a higher concentration due to the membrane rejection of particles. The diluted water is transmitted only if the hydraulic pressure difference between the feed side and the permeate side ($\Delta P = P_f - P_p$) is higher than the osmotic pressure difference between these sides ($\Delta\pi = \pi_f - \pi_p$). Both membrane total area and its permeability are important to be considered in the model. The following assumptions are taken for the model:

1. The water permeability coefficient (A) is assumed to be constant.
2. The concentration polarization effect is ignored.
3. The hydraulic pressure loss as the fluid flows through the channels is negligible.
4. The permeate osmotic pressure is constant across the channel.
5. The osmotic pressure is linearly proportional to the salinity due to van't Hoff's equation.

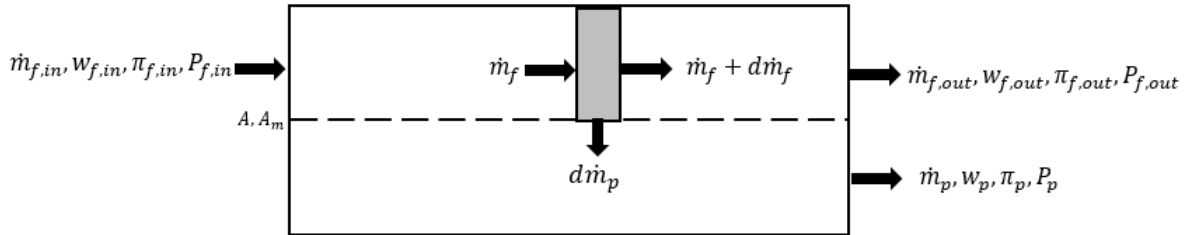


Fig. 2-2. Schematic drawing of a membrane-based NF mass exchanger

2.2.1. Mathematical modelling

a. Water flow

The SDM model provides equation (2.1) that expresses the differential permeate flow rate of the transmitted water through the differential membrane area.

$$d\dot{Q}_p = K_w(\Delta P - \Delta\pi) dA_m \quad (2.1)$$

where,

$\dot{Q}_p$, is the permeate flow rate (m^3/s)

K_w , is water permeability coefficient ($m^3/m^2\cdot s\cdot kPa$)

ΔP , is the hydraulic pressure difference across the two streams (kPa)

$\Delta\pi$, is osmotic pressure difference across the two streams (kPa)

A_m , is the surface area of the membrane (m^2)

Dividing both sides of Eq. (2.1) by the permeate density gives the differential permeate mass flow rate.

$$d\dot{m}_p = A(\Delta P - \Delta\pi) dA_m \quad (2.2)$$

where, $\dot{m}_p$, is the permeate mass flow rate, in (kg/s), and A , is the modified water permeability coefficient in ($kg/m^2\cdot s\cdot kPa$). The osmotic pressure can be determined using the following equation:

$$\pi = \phi RT \rho_{solvent} \sum_{j=solution} b_j \quad (2.3)$$

where ϕ is the osmotic coefficient, R is the universal gas constant, T is feed stream absolute temperature, ρ is water density, and $\sum_{j=solution} b_j$ is the summation of molarities of all ionic and non-ionic constituents in the water. The relation of the osmotic pressure in Eq. (2.3) with the salinity is shown to be nonlinear. To facilitate the analytical work, the osmotic pressure is

linearized using the van't Hoff equation. The linear osmotic pressure equation as a function of salinities is expressed as:

$$\Delta\pi = \pi_f - \pi_p = C(w_f - w_p) \quad (2.4)$$

where w (g/kg) is the concentration of salts in water, C is the modified van 't Hoff's coefficient [12]. Substituting Eq. (2.4) into Eq. (2.2), we get

$$d\dot{m}_p = A \left(\Delta P - C(w_f - w_p) \right) dA_m \quad (2.5)$$

Since the concentration of the feed is changing while it flows, the conservation of solutes between the inlet feed salinity and any other location along the channel will be:

$$\dot{m}_{s,f} = \dot{m}_{f,in} w_{f,in} = \dot{m}_f w_f + \dot{m}_p w_p \quad (2.6)$$

The change in the feed mass is expressed as the following conservation equation:

$$\dot{m}_{f,in} = \dot{m}_f + \dot{m}_p \quad (2.7)$$

Substitution of Eq. (2.7) into Eq. (2.6) yields:

$$w_f = \frac{\dot{m}_{f,in} w_{f,in} - \dot{m}_p w_p}{\dot{m}_{f,in} - \dot{m}_p} \quad (2.8)$$

Substituting Eq. (2.8) into Eq. (2.5) gives the following equation:

$$d\dot{m}_p = A \left(\Delta P - C \left(\frac{\dot{m}_{f,in} w_{f,in}}{\dot{m}_{f,in} - \dot{m}_p} - \frac{\dot{m}_p w_p}{\dot{m}_{f,in} - \dot{m}_p} - w_p \right) \right) dA_m \quad (2.9)$$

Now, the required dimensionless quantities will be defined:

The recovery ratio (RR) is the fraction of the produced flow rate to the feed flow rate. It can be used to show and evaluate the performance of an NF system.

$$RR = \frac{\dot{m}_p}{\dot{m}_{f,in}} \quad (2.10)$$

The feed osmotic pressure ratio (SR_f) is the ratio of the feed osmotic pressure at the entrance of the system to the difference of the hydraulic pressure.

$$SR_f = \frac{\pi_{f,in}}{\Delta P} \quad (2.11)$$

It should be noted that since the osmotic pressure is lower than the hydraulic pressure, this ratio must always be less than one. The permeate osmotic pressure ratio (SR_p) is the ratio of the permeate osmotic pressure to the difference of the hydraulic pressure.

$$SR_p = \frac{\pi_p}{\Delta P} \quad (2.12)$$

The number of transfer units (NTU) of the heat exchanger is used to make an analogy to the dimensionless parameter MTU for a NF mass exchanger. The mass transfer units is found to be (See the Appendix for derivation):

$$MTU = \frac{AA_m \Delta P}{\dot{m}_{f,in}} \quad (2.13)$$

Now, dividing both sides of Eq. (2.9) by the entrance feed rate ($\dot{m}_{f,in}$) and applying the non-dimensional Eqs. (2.10)-(2.13) leads to the following equation:

$$dRR = \left(1 - \frac{SR_f}{1 - RR} + RR \frac{SR_p}{1 - RR} + SR_p \right) dMTU \quad (2.14)$$

The boundary condition is that, at the inlet, $MTU = 0$ when $RR = 0$. The integration of Eq. (2.14) can be taken with the assumption of neglecting the pressure drop along the channel.

$$MTU = \int_0^{RR} \left(1 - \frac{SR_f}{1 - RR} + RR \frac{SR_p}{1 - RR} + SR_p \right)^{-1} dRR \quad (2.15)$$

Integration of Eq. (2.15) yields:

$$MTU = RR + (SR_f - SR_p) \ln \left(\frac{SR_f - SR_p - 1}{RR + SR_f - SR_p - 1} \right) \quad (2.16)$$

This relation helps in designing the membrane of a NF mass exchanger by determining its effective surface area using the required mass transfer units.

Using the mass and salt balance equations (2.6 - 2.7) and the introduced non-dimensional terms Eqs. (2.10 - 2.12), the brine salinity at the outlet of the feed channel is expressed as below:

$$w_{f,out} = w_{f,in} \frac{1 - RR \left(\frac{SR_p}{SR_f} \right)}{1 - RR} \quad (2.17)$$

Then, the concentration factor (*CF*) can be defined as the ratio of the brine to source water salinities.

$$CF = \frac{w_{f,out}}{w_{f,in}} = \frac{1 - RR \left(\frac{SR_p}{SR_f} \right)}{1 - RR} \quad (2.18)$$

The concentration factor expresses how many times the brine is more concentrated with respect to the feed. It is an important parameter to consider in designing a desalination system since high *CF* numbers may lead to salt precipitation and scale formation.

b. Salt flow

It is important to analyse and study the transport of the salt through NF membrane. Salt flow, according to the SDM model, is modelled based on the integration of ion adsorption and diffusion within the membrane. The SDM model provides the following equation that expresses the differential salt rate transported through the differential membrane area [50].

$$d\dot{m}_s = K_s(\Delta c_s) dA_m \quad (2.19)$$

where,

$\dot{m}_s$, is the salt flow rate (g/s)

K_s , is membrane permeability coefficient for salt ($m^3/m^2 \cdot s$)

Δc_s , is salt concentration differential across membrane (g/m^3)

Multiplying salt permeability and dividing the salt concentration differential by the density (ρ) gives:

$$d\dot{m}_s = A_s(w_f - w_p) dA_m \quad (2.20)$$

Where, A_s , is the modified salt permeability coefficient in ($kg/m^2 \cdot s$). The feed salinity equation (Eq. 2.8) is applied to Eq. 2.20.

$$d\dot{m}_s = A_s \left(\frac{\dot{m}_{f,in} \times w_{f,in} - \dot{m}_p \times w_p}{\dot{m}_{f,in} - \dot{m}_p} - w_p \right) dA_m \quad (2.21)$$

Dividing both sides by feed mass flow rate ($\dot{m}_{f,in}$) and feed salinity ($w_{f,in}$), and manipulating the equation with water permeability, A_w , and applying the non-dimensional Eqs. (2.10)-(2.13) lead to the following equation:

$$\frac{d\dot{m}_s}{\dot{m}_{f,in} w_{f,in}} = \frac{A_s}{A_w (C w_{f,in})} \left(\frac{\frac{C w_{f,in}}{\Delta P}}{1 - \frac{\dot{m}_p}{\dot{m}_{f,in}}} - \frac{\frac{\dot{m}_p}{\dot{m}_{f,in}} \times \frac{C w_p}{\Delta P}}{1 - \frac{\dot{m}_p}{\dot{m}_{f,in}}} - \frac{C w_p}{\Delta P} \right) \left(\frac{A_w \Delta P dA_m}{\dot{m}_{f,in}} \right) \quad (2.22)$$

Or,

$$\frac{d\dot{m}_s}{\dot{m}_{s,f}} = \frac{A_s}{A_w \pi_{f,in}} \left(\frac{SR_f}{1-RR} - \frac{RR \times SR_p}{1-RR} - SR_p \right) dMTU \quad (2.23)$$

New non-dimensional groups can be defined as the following:

The salt transport ratio (ST_s) is the fraction of the transport salt flow rate to the feed salt flow rate.

$$ST_s = \frac{\dot{m}_s}{\dot{m}_{s,f}} \quad (2.24)$$

Also, the permeability-feed osmotic pressure ratio is defined as the following:

$$\lambda_o = \frac{A_s/A_w}{\pi_{f,in}} \quad (2.25)$$

Applying the new non-dimensional groups (Eq. 2.24, and Eq. 2.25) to Eq. (2.23) yields:

$$dST_s = \lambda_o \left(\frac{SR_f}{1-RR} - \frac{RR \times SR_p}{1-RR} - SR_p \right) dMTU \quad (2.26)$$

The boundary condition is that, at the inlet, $MTU = 0$ when $ST_s = 0$. The integration of Eq. (2.26) can be taken as:

$$MTU = \int_0^{ST_s} \left[\lambda_o \left(\frac{SR_f}{1-RR} - \frac{RR \times SR_p}{1-RR} - SR_p \right) \right]^{-1} dST_s \quad (2.27)$$

Integration of Eq. (2.27) yields:

$$MTU = \frac{ST_s(1-RR)}{\lambda_o(SR_f - SR_p)} \quad (2.28)$$

Or:

$$ST_s = \frac{\lambda_o(SR_f - SR_p)}{1-RR} MTU \quad (2.29)$$

Applying MTU model equation (Eq. 2.16) to salt transport equation shows the parameters that salt transport depends on.

$$ST_s = \lambda_o \frac{(SR_f - SR_p)}{1-RR} \left[RR + (SR_f - SR_p) \ln \left(\frac{SR_f - SR_p - 1}{RR + SR_f - SR_p - 1} \right) \right] \quad (2.30)$$

2.2.2 Results and discussion

Figs. 2-3 (a)-(d) show the relation of the recovery ratio with the mass transfer units at different osmotic pressure ratios. The osmotic pressures are taken to be linear with the salinities of the stream at a temperature of 25 °C.

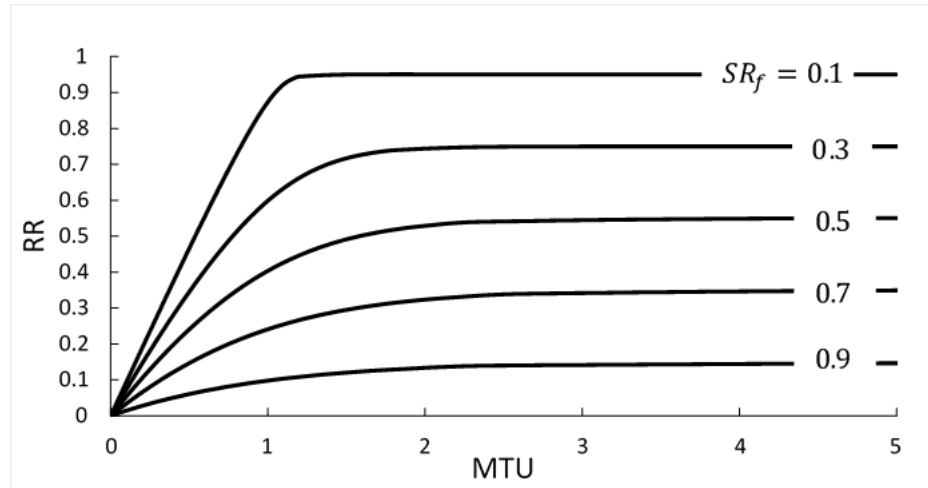


Fig. 2-3(a). Variation of recovery ratio with respect to MTU at different osmotic pressure ratios ($SR_p = 0.05$).

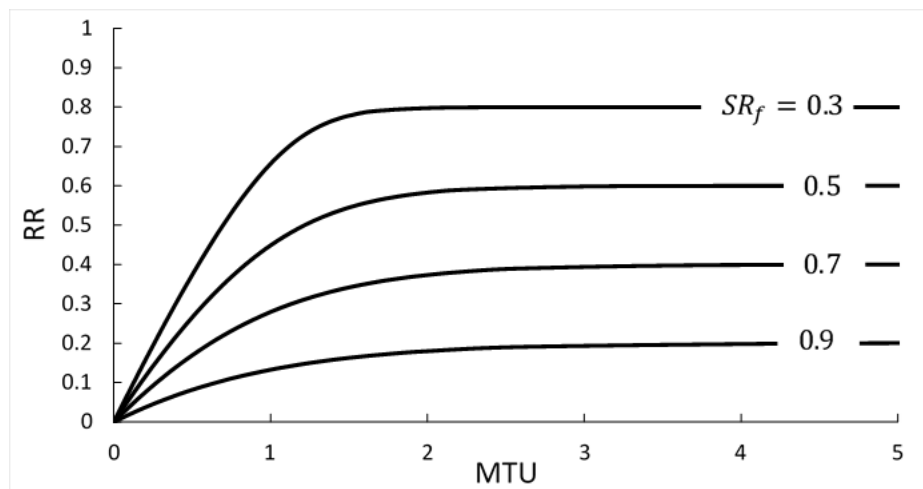


Fig. 2-3(b). Variation of recovery ratio with respect to MTU at different osmotic pressure ratios ($SR_p = 0.1$)

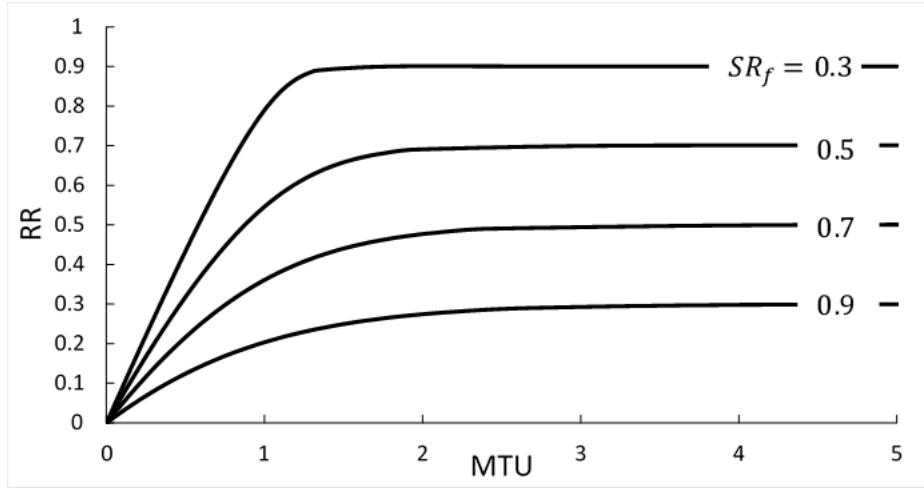


Fig. 2-3(c). Variation of recovery ratio with respect to MTU at different osmotic pressure ratios ($SR_p = 0.2$)

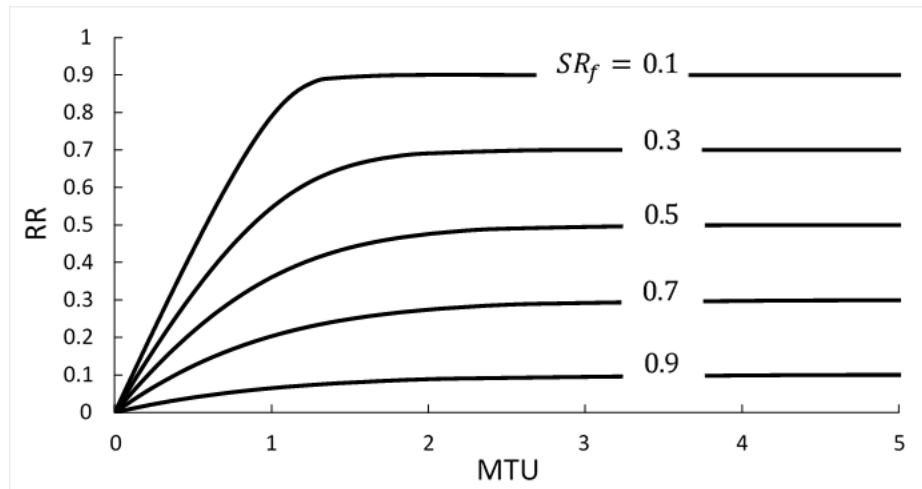


Fig. 2-3(d). Variation of recovery ratio with respect to MTU at different osmotic pressure ratios ($SR_p = 0$)

It can be seen from Fig. 2-3(a) that at high MTU values of $SR_f = 0.1$, the brine salinity will be high enough so that the osmotic pressure deviates from linearity. However, the typical recovery ratio rates of NF technology are lower and in the range that keeps the osmotic pressure behavior as linear. Figs. 2-3(b, c) show the variation of the MTU with the recovery ratios for different permeate osmotic pressures ratios. It can be noted that as the permeate osmotic pressure ratio increases, the related recovery ratio increases at a certain MTU value. In other words, having a higher SR_p leads to a lower osmotic pressure difference, so the net driving pressure (NDP) will be higher at some fixed hydraulic pressure value, leading to more recovered water. In Fig. 2-3(d), the relationship between the recovery ratio and the mass transfer units is illustrated, assuming no salt in the permeate ($SR_p = 0$). It provides an exact match for a RO mass exchanger that was shown by Banchik [12] since he assumed ideal membranes with 100% salt rejection. As a general comparison, it is found that, a $SR_p = 0.05$, which was the maximum value in the design examples, will result in decreasing the MTU needed to obtain the same recovery ratio for the RO mass exchanger model ($SR_p = 0$) by 6% to 60%. Therefore, it may also be said that the NF mass exchanger model can be considered as a more general case where the design is dependent on the salinity of the product water, demonstrating the need for considering the product salinity for greater accuracy.

Figs. 2-4(a, b) show a relation between the brine concentration of seawater and brackish water feed inlet salinities, respectively. It is noted in both figures that at $SR_f = 0.1$, the salinity of the brine is very high at high MTU. However, NF exchangers are not intended to operate at recovery ratios that result in these high brine concentrations due to the limitations of the system.

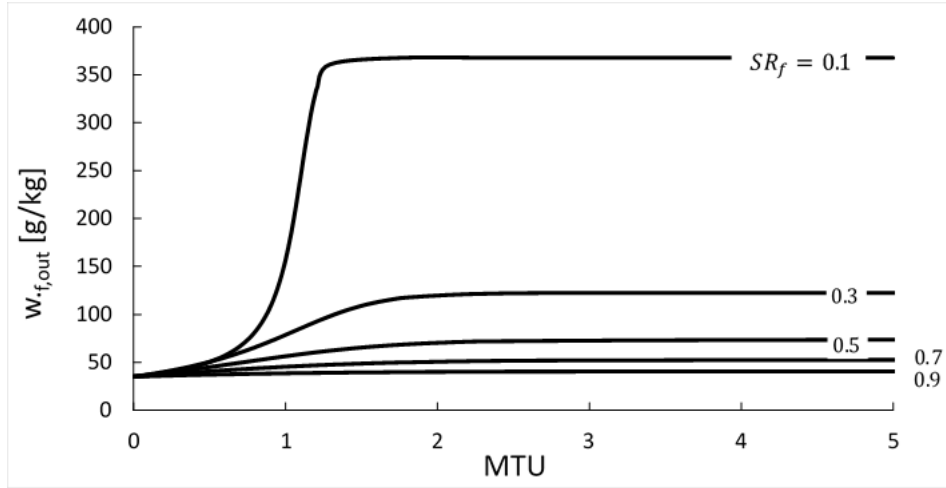


Fig. 2-4(a). Variation of seawater brine salinity against MTU at different osmotic pressure ratios ($SR_p = 0.05$). The inlet feed salinity is $w_{f,in} = 35$ g/kg

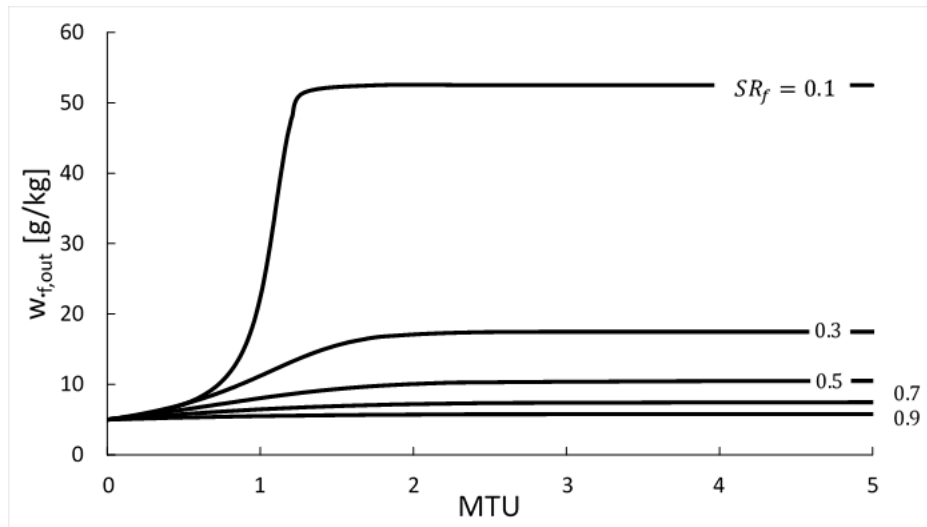


Fig. 2-4(b). Variation of brackish water brine salinity against MTU at different osmotic pressure ratios ($SR_p = 0.05$). The inlet feed salinity is $w_{f,in} = 5$ g/kg

For seawater desalination, CF is mostly between 1.7-2 and rarely goes more than 3, while CF for brackish water desalination can reach higher values depending on the feed. The concentration factor as a function of the mass transfer units is plotted in Fig. 2-5 for different osmotic pressure ratios.

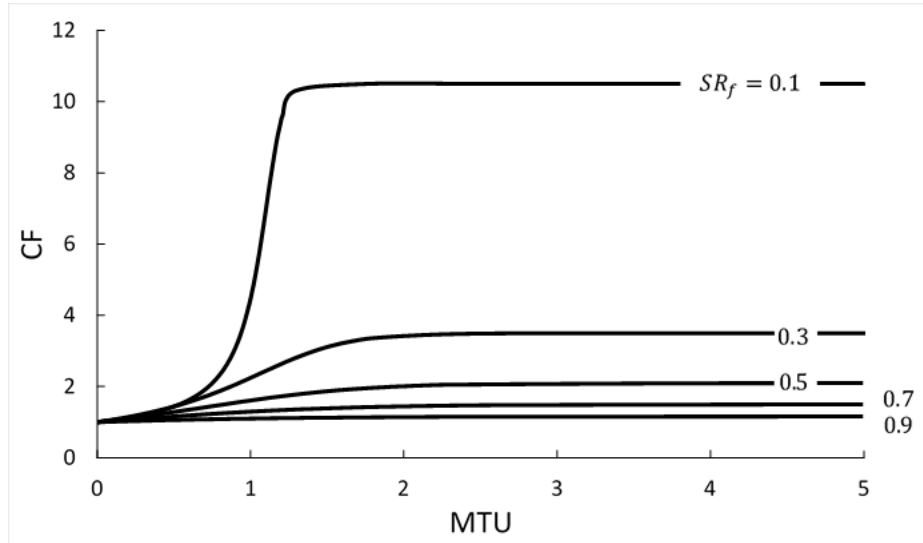


Fig. 2-5. Variation of concentration factor with respect to the MTU at different osmotic pressure ratios ($SR_p = 0.05$)

It shows that when a system has a high concentration factor, it will require a higher MTU value to achieve a desired level of desalination. The concentration near the surface of the membrane increases as the concentration factor increases, which leads to a higher driving force and MTU needed to transfer the water. The figure also shows the effect of the feed osmotic pressure ratio on CF. As its value becomes smaller, the higher the salinity factor and, thus, the MTU is higher. It is noted in the figure that, at $SR_f = 0.1$, the concentration factor is very high at high MTU indicating a large membrane area requirement and cost.

The relationship between NF salt transport ratio, ST_s , and mass transfer units, MTU , is shown in Figs. 2-6 with assuming a value of 0.06 for the permeability-feed osmotic pressure ratio, λ_o , and permeate osmotic pressure ratio of $SR_p = 0.05$. The figure relates the salt transport through the membrane directly with MTU. The figure trends also help the designer to understand the salt relations and figure out the proper feed osmotic pressure needed to have the least salt transported.

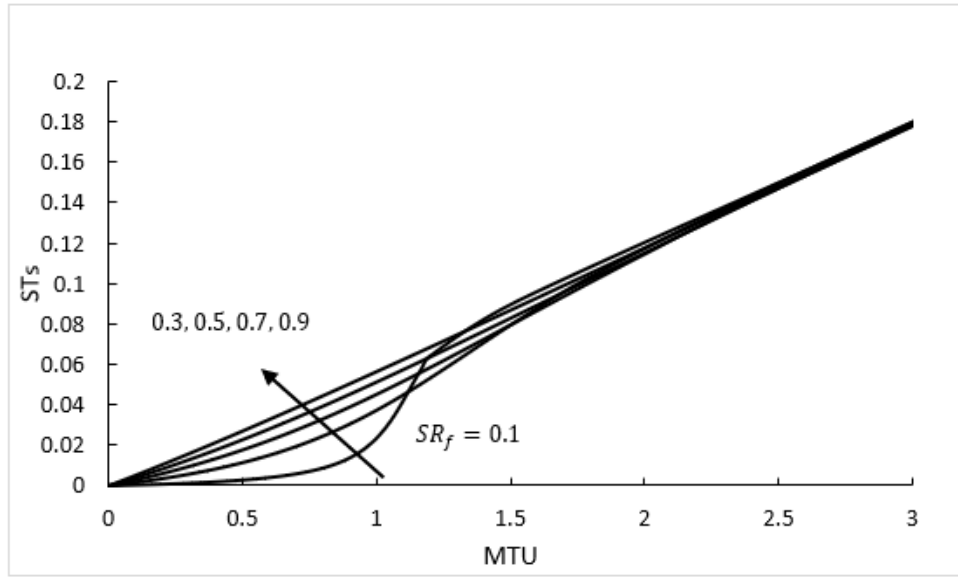


Fig. 2-6. Variation of Salt transport ratio with respect to MTU at different osmotic pressure ratios ($SR_p = 0.05$).

It is also noted from the figure that as the system recovery ratio is approaching its maximum value, and the permeability-feed osmotic pressure ratio is approaching unity, the salt transport ratio values converge to be equal to MTU value. This can also be mathematically demonstrated.

$$ST_s = \frac{\lim_{\lambda_o \rightarrow 1} \lambda_o (SR_f - SR_p)}{1 - \lim_{RR \rightarrow RR_{max}} RR} MTU \quad (2.31)$$

Using maximum recovery ratio equation, leads to:

$$ST_s \equiv MTU \quad (2.32)$$

Permeate salinity is also affected by the value of MTU. Increasing the MTU generally implies improving the mass transfer efficiency, which, in the case of NF, often leads to a reduction in permeate salinity. Fig. 2-7 shows the relation between permeate osmotic pressure ratio and MTU. The figure shows the relationship between the SR_p and MTU for feed osmotic pressure ratios

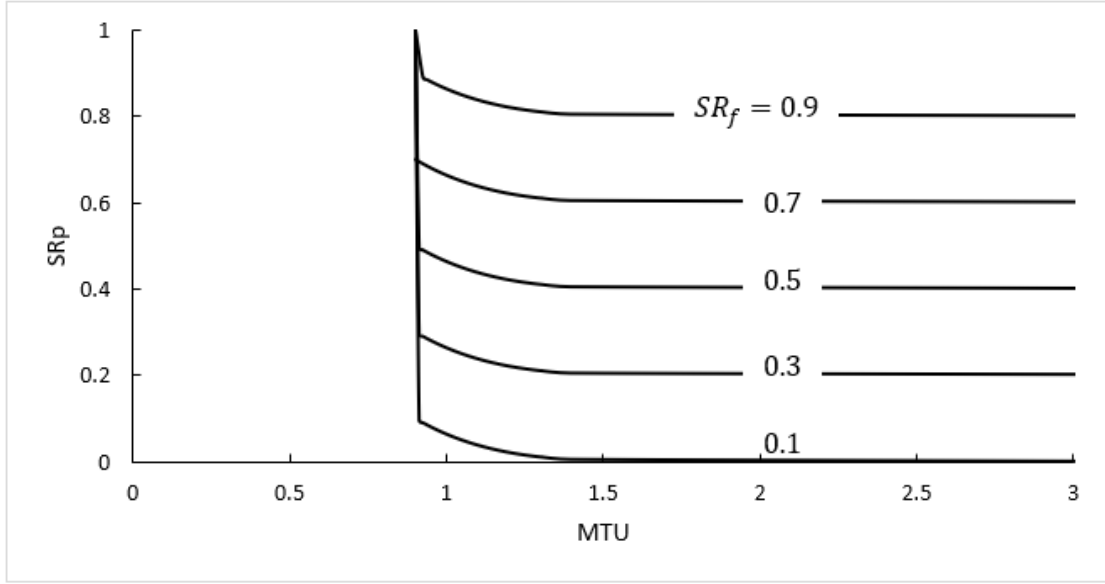


Fig. 2-7. Variation of permeate osmotic ratio with respect to the MTU at different osmotic pressure ratios ($RR = 0.9$)

(SR_f) at $RR = 0.9$. This diagram is a comprehensive drawing of all possible states of NF mass exchange at this value of feed osmotic pressure (i.e. $0 < SR_p < SR_f = 0.1$), depending on membrane specifications and its permeabilities. It shows the extent of the effect of MTU on the degrees of salinity of the produced water. So, the designer must balance between all the parameters, which can be used by manipulating the value of MTU. Salt Passage, SP , is the amount of salt that passes through an NF membrane during the process. It is the ratio of the salt concentration in the product water over the salt concentration in the feed water [51].

$$SP = \frac{w_p}{w_{f,in}} = \frac{SR_p}{SR_f} \quad (2.33)$$

Salt rejection is an important parameter as a way to show how efficient NF membranes are in preventing salt passage from the feed stream to the permeate stream. The higher the salt rejection, the more effective the membrane is at purifying the feed [52].

$$S_{rej} = 1 - SP = 1 - \frac{SR_p}{SR_f} \quad (2.34)$$

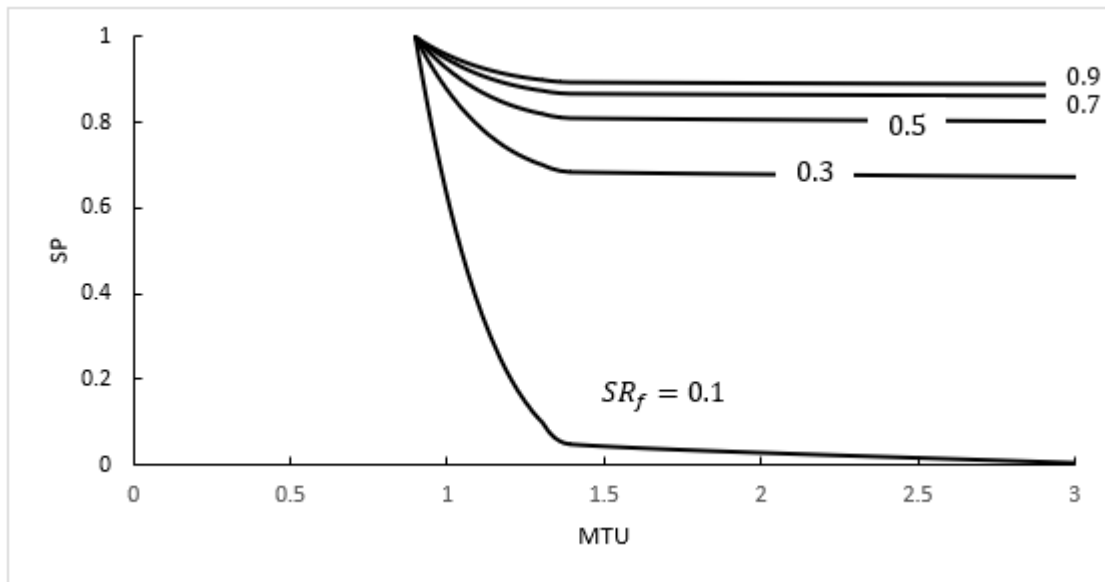


Fig. 2-8. Variation of salt passage with respect to the MTU at different osmotic pressure ratios (RR = 0.9)

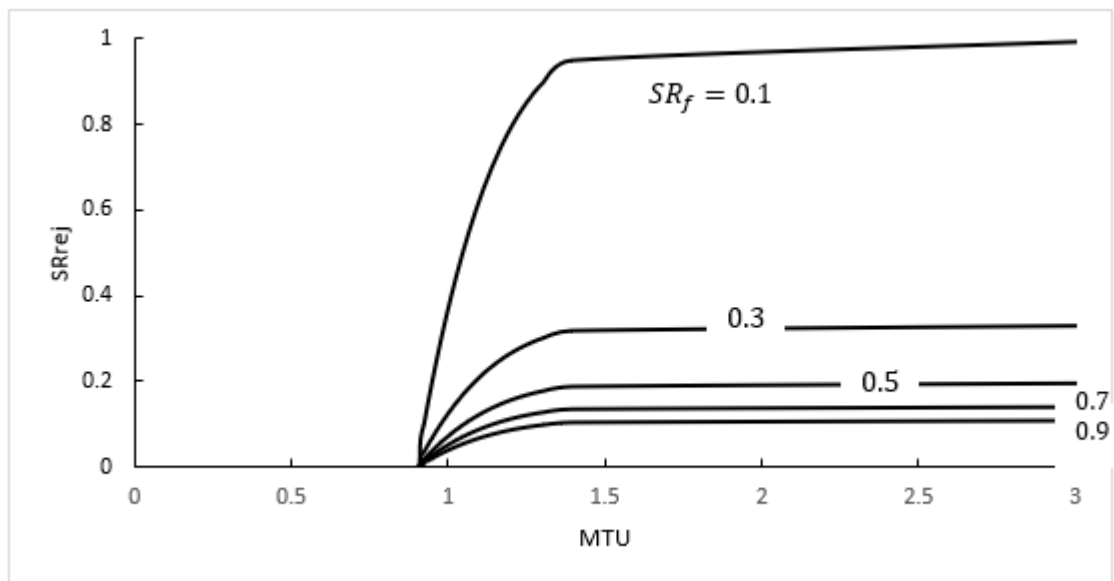


Fig. 2-9. Variation of salt rejection with respect to the MTU at different osmotic pressure ratios (RR = 0.9)

Fig. 2-8 and Fig. 2-9 show the variation of salt passage and salt rejection with MTU, respectively. As MTU increases, salt passage typically decreases. A higher MTU signifies a more effective barrier to salt transfer since a higher transfer rate of water is taken, resulting in lower salt passage and, consequently, lower salinity in the permeate, w_p .

2.3. Nanofiltration effectiveness (ε -MTU model)

The effectiveness of a NF system can be defined as the ratio of the actual permeate flow rate produced by a certain size of the mass exchanger to the maximum possible permeate flow rate for a given applied hydraulic pressure and an inlet feed osmotic pressure. This allows the definition also to be the actual recovery ratio of the system to the maximum recovery ratio (See Eq. (2.35)). For each value of the osmotic ratio, there is a certain maximum recovery ratio that is achieved as the MTU value increases, as shown in Fig. 2-3. Furthermore, the effectiveness can reach to a maximum of 1.

$$\varepsilon = \frac{RR}{RR_{\max}} \quad (2.35)$$

The maximum recovery ratio is reached by the maximum permeate flow rate that is achieved when the pressure differences ($\Delta P - \Delta \pi$) reaches zero since the osmotic pressure increases to the point where it equals the hydraulic pressure at the outlet of the mass exchanger. i.e.

$$\Delta P = \Delta \pi = \pi_{f,out} - \pi_p \quad (2.36)$$

Using the mass and salt balance equations (2.5), (2.6), Eq. (2.37) gives the following expression:

$$RR_{\max} = 1 - SR_f + SR_p \quad (2.37)$$

Substituting Eqs. (2.17), (2.38) into Eq. (2.14) leads to an expression for MTU as a function of the effectiveness.

$$MTU = \varepsilon(1 - SR_f + SR_p) - (SR_f - SR_p) \ln(1 - \varepsilon) \quad (2.38)$$

2.3.1. Results and discussion

Fig. 2-10 shows the variation of the effectiveness with the MTU at various feed osmotic pressures. For low values of MTU, the effectiveness is approximately equal to the MTU. This can be proven mathematically since the derivative of the MTU with respect to ε approaches 1 for small values of the MTU and effectiveness (See Eqs. (2.25)- (2.26) below).

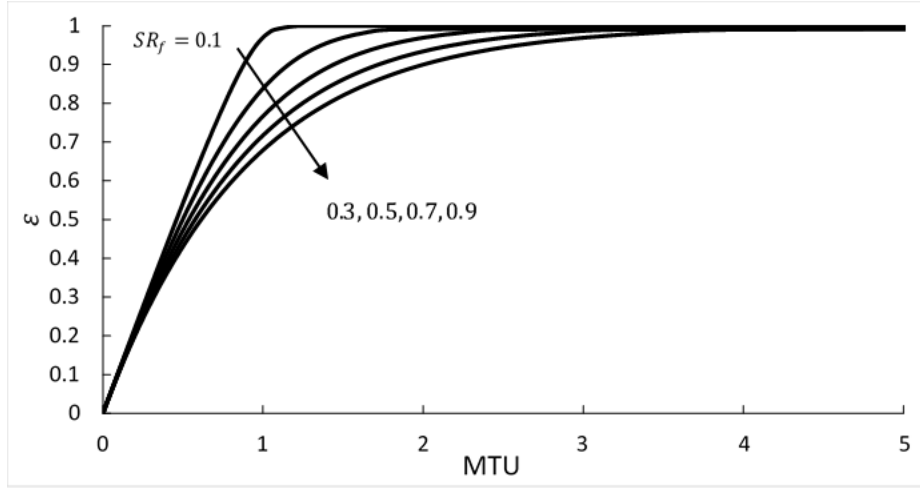


Fig. 2-10. Variation of effectiveness with respect to MTU at different feed osmotic pressures ($SR_p = 0.05$)

$$\lim_{\varepsilon \rightarrow 0} \frac{dMTU}{d\varepsilon} = \lim_{\varepsilon \rightarrow 0} \left(1 - SR_f + SR_p + \frac{SR_f - SR_p}{1 - \varepsilon} \right) = 1 \quad (2.39)$$

It is clear from Eq. (2.39) that, at $MTU \ll 1$, the effectiveness equals the MTU. This result can also be found by considering the integrated form of the zero-dimensional form of the permeate mass flow rate i.e. Eq. (2.2), and substituting Eq. (2.35) and Eq. (2.37) such that at $MTU \ll 1$,

$$\varepsilon = \frac{RR_{zero-dimensional}}{RR_{max}} = \frac{AA_m (\Delta P - \Delta \pi)}{\dot{m}_f \left(1 - \frac{\pi_{f,in}}{\Delta P} + \frac{\pi_p}{\Delta P} \right)} = MTU \quad (2.40)$$

This result shows an analogy with the limit for heat exchangers where the effectiveness and NTU are equal as NTU approaches zero [53]. Moreover, the maximum effectiveness is reached by the maximum permeate flow rate that is achieved when the pressure differences ($\Delta P - \Delta \pi$) reaches zero.

$$\Delta P - \Delta \pi = 0 \quad (2.41)$$

Applying the nondimensional parameters Eq. (2.11) and Eq. (2.12) to Eq. (2.42) yields

$$1 - SR_f + SR_p = 0 \quad (2.42)$$

Using Eq. (2.42) to the case of the maximum effectiveness point of the mass exchanger by applying it to Eq. (2.38) gives:

$$\varepsilon = 1 - e^{-MTU} \quad (2.43)$$

This equation shows an analogy to the heat exchanger effectiveness equation as the maximum heat capacity approaches infinity [54].

$$\varepsilon = 1 - e^{-NTU} \quad (2.44)$$

It can be noted that to obtain high effectiveness, the system must have the lowest possible osmotic pressure ratios at a specified MTU value to obtain the required outputs, especially at MTU values greater than 0.4 where it shows the onset of the effect of the osmotic pressure ratios. Furthermore, when designing the NF mass exchanger, the osmotic pressure ratios affect the MTU value if the engineer is required to design the system at a certain effectiveness. For example, when the effectiveness is 60% and $SR_f = 0.1$, the MTU value for this design will be 0.56 while, for $SR_f = 0.9$, the MTU value will be 0.81, which implies a 30% higher membrane area required to achieve the specified effectiveness.

2.4. Design Examples

2.4.1. Designing high-quality drinking water NF plant

Costa and De Pinho [55] designed a NF plant to produce high-quality drinking water. The objective is to find the total required membrane area to produce a total permeate flow rate of 1157.4 kg/s . Tagus River water was used as a source for the feed. NF200B-400 membranes were used in the system. The feed is diluted in three stages containing a total of 4302 pressure vessels. The membrane and operation input data are as follows:

Membrane salt rejection is 86%

Water permeability (A) is $1.889 \times 10^{-5} \text{ kg/m}^2\text{-s-kPa}$

- For the first stage:

Feed pressure (P_f) is 600 kPa

Inlet feed flow rate ($\dot{m}_{f,in}$) is 1273.8 kg/s

Inlet feed salinity (w_f) is $3.2 \times 10^{-3} \text{ g/kg}$

Recovery ratio (RR) is 0.36

- For the second stage:

Feed pressure (P_f) is 600 kPa

Inlet feed flow rate ($\dot{m}_{f,in}$) is 825 kg/s

Inlet feed salinity (w_f) is $4.8 \times 10^{-3} \text{ g/kg}$

Recovery ratio (RR) is 0.71

- For the third stage:

Feed pressure (P_f) is 550 kPa

Inlet feed flow rate ($\dot{m}_{f,in}$) is 534.6 kg/s

Inlet feed salinity (w_f) is 7.2×10^{-3} g/kg

Recovery ratio (RR) is 0.9

Solution using the model:

The feed salinities of each stage are used to calculate the osmotic pressure ratio.

$$SR_{f,(stage\ 1)} = \frac{\pi_{f,in}}{\Delta P} = \frac{Cw_{f,in}}{\Delta P} = \frac{73.45 \times (2 \times 10^{-3})}{(600 - 101)} = 4.71022 \times 10^{-4}$$

Permeate salinity is found using the salt rejection, (w_p) is 3.56×10^{-4} g/kg. So, permeate osmotic pressure ratio is:

$$SR_{p,(stage\ 1)} = \frac{\pi_p}{\Delta P} = \frac{Cw_p}{\Delta P} = \frac{73.45 \times (6 \times 10^{-4})}{(600 - 101)} = 5.299 \times 10^{-5}$$

Using the same method, the osmotic pressure ratios for the other stages are:

$$SR_{f,(stage\ 2)} = 7.065 \times 10^{-4}, \quad w_{p,2} = 3.82 \times 10^{-3} \text{ g/kg}, \quad SR_{p,(stage\ 2)} = 5.622 \times 10^{-5}$$

$$SR_{f,(stage\ 3)} = 1.118 \times 10^{-3}, \quad w_p = 1.65 \times 10^{-4} \text{ g/kg}, \quad SR_{p,(stage\ 3)} = 1.65 \times 10^{-4}$$

Equation (2.16) or Fig. 2-3 can be used to find the MTU of each stage:

$$MTU_{stage\ 1} = 0.3603, \quad MTU_{stage\ 2} = 0.7102, \quad MTU_{stage\ 3} = 0.9$$

Thus, using the definition of MTU as in Eq.(2.13), the total membrane area of each stage:

$$A_{m,1} = \frac{\dot{m}_{f,in,1} \times MTU_1}{\Delta P \times A} = \frac{1273.8 \times 0.3603}{499 \times 1.889 \times 10^{-5}} = 48671.94 \text{ m}^2$$

$$A_{m,2} = \frac{\dot{m}_{f,in,2} \times MTU_2}{\Delta P \times A} = \frac{825 \times 0.7102}{499 \times 1.889 \times 10^{-5}} = 62153.45 \text{ m}^2$$

$$A_{m,3} = \frac{\dot{m}_{f,in,3} \times MTU_3}{\Delta P \times A} = \frac{534.6 \times 0.9}{449 \times 1.889 \times 10^{-5}} = 56878.38 \text{ m}^2$$

So, the total membrane area required for the production is found to be $A_m = 167703 \text{ m}^2$. Costa and De Pinho [55] found the total area to be 159094 m^2 . Therefore, the error with respect to calculated area is 5.42%, which is reasonable.

2.4.2. Designing NF plant to produce reusable water of a factory

Riera et al. [56] designed a NF plant to obtain reusable water. The objective is to find the total required membrane area to produce a total permeate flow rate of 4.861 kg/s . The feed of the plant is the industrial used water of a dairy factory. The membrane and operation input data are as follows:

Feed pressure (P_f) is 2500 kPa

Inlet feed salinity (w_f) is 0.1728 g/kg

Permeate salinity is (w_p) 0.0472 g/kg

Water permeability (A) is $1.11 \times 10^{-5} \text{ kg/m}^2\text{-s-kPa}$

Recovery ratio (RR) is 0.875

Solution using the model:

$$SR_f = \frac{\pi_{f,in}}{\Delta P} = \frac{Cw_{f,in}}{\Delta P} = \frac{73.45 \times (0.1727)}{(2500 - 101)} = 5.29 \times 10^{-3}$$

$$SR_p = \frac{\pi_p}{\Delta P} = \frac{Cw_p}{\Delta P} = \frac{73.45 \times (0.0472)}{(2500 - 101)} = 1.445 \times 10^{-3}$$

By following the same procedure as in the previous example and using Eq. (2.16) or Fig. 2-3, the MTU is found to be 0.8831. This gives, using Eq. (2.8), a total membrane area $A_m = 184.056 \text{ m}^2$. Riera et al. [56] proposed a NF plant with an area of 185.4 m^2 to treat the required condensates. The error of the ε -MTU model is found to be 0.73% in this case.

2.4.3. Red Sea water NF plant (Umm Lujj SWNF plant simulation)

Palmeri et al. [57] were able to simulate a single-stage NF plant using the NanoFlux program. This stage is used as pre-treatment for a seawater RO feed stream. They were able to determine the total area needed to produce 71.11 kg/s . The membrane and operation input data are as follows:

Feed pressure (P_f) is 2500 kPa

Permeate pressure (P_p) is 101 kPa

Inlet feed flow rate ($\dot{m}_{f,in}$) is 100 kg/s

Inlet feed salinity (w_f) is 41.4 g/kg

The salt rejection is 28% ($w_p = 29.81 \text{ g/kg}$)

Water permeability (A) is $1.028 \times 10^{-5} \text{ kg/m}^2\text{-s-kPa}$

Solution using the model:

The recovery ratio is found to be:

$$RR = \frac{\dot{m}_p}{\dot{m}_{f,in}} = 0.711$$

The concentrations are used to calculate the osmotic pressure ratio:

$$SR_f = \frac{\pi_{f,in}}{\Delta P} = \frac{C w_{f,in}}{\Delta P} = \frac{76.76 \times 41.4}{2399} = 1.325$$

$$SR_p = \frac{\pi_p}{\Delta P} = \frac{C w_p}{\Delta P} = \frac{73.45 \times 29.81}{2399} = 0.913$$

Eq. (2.16) or Fig. 2-3 can be used to find the MTU as 1.355, such that the total area of the NF plant is determined to be 5496 m^2 using the ε -MTU model. Palmeri et al. [57] found the area to be 5268 m^2 . The error incurred by our model is, therefore, 4.33%, which can be due to the high feed salinity since it makes the osmotic pressure deviate from linearity.

2.4.4. NF for brackish water, the textile effluent in Tunisia

Palmeri et al. [57] were also able to simulate another NF plant using the NanoFlux program. The NF plant is used for water treatment of textile wastewater of a factory in Tunisia that deals with dyeing, gluing, and finishing. They were able to have the area needed to have diluted water flow rate as 17.437 kg/s . The membrane and operation input data are as follows:

Feed pressure (P_f) is 2000 kPa

Inlet feed flow rate ($\dot{m}_{f,in}$) is 27.22 kg/s

Inlet feed salinity (w_f) is 7.5 g/kg

permeate salinity (w_p) is 1.4 g/kg

Water permeability (A) is $1.461 \times 10^{-5} \text{ kg/m}^2\text{-s-kPa}$

Solution using the model:

The recovery ratio can be found as:

$$RR = \frac{\dot{m}_p}{\dot{m}_{f,in}} = 0.6405$$

The concentrations are used to calculate the osmotic pressure ratio.

$$SR_f = \frac{C w_{f,in}}{\Delta P} = \frac{73.45 \times 7.5}{1899} = 0.3$$

$$SR_p = \frac{C w_p}{\Delta P} = \frac{73.45 \times 1.4}{1899} = 0.055$$

Equation (2.16) or Fig. 2-3 can be used to find the MTU to be 1.12, so that the membrane area is determined to be 1110 m^2 using the ε -MTU model. Palmeri et al. [57] found the area to be 1170 m^2 . The error in the calculation of the area is, therefore, 5.13%.

2.5. Conclusion

A closed-form analytical solution for a one-dimensional NF mass exchanger is developed based on an analogy with heat exchangers. The membrane recovery ratio varies with three introduced nondimensional groups, which are the mass transfer units and both feed and dilute osmotic pressure ratios. The ε -MTU model is developed under the assumption of the linearity of the osmotic pressure ratio for the salinities of both streams. The model is applied to several existing large-scale plants designed with both measured and non-linear calculated osmotic pressures, and the results are compared. The error between the ε -MTU model and the designed plants is found to range from 0.73% to 5.42%, while the average error was 3.9%. Finally, since the permeate salinity is taken into account, it is a more general case in the sense that the developed model also applies to a RO mass exchanger.

Chapter 3

Analogy of Electrodialysis Mass Exchangers to Heat Exchanger

Chapter Abstract:

Heat exchangers and electrodialysis (ED) systems share a strong analogy. A method similar to ε -NTU is developed for designing ED mass exchangers that can be called ε -MTU (effectiveness-mass transfer units). This method is used to relate some membrane and operation parameters (such as the size, applied voltage, salinities, etc) to the transport ratio and the effectiveness parameter resulting in a closed form solution. The governing equations are non-dimensionalized under appropriate assumptions such as the current density always being lower than the limiting current density. The effectiveness of the ED mass exchanger is defined as the system transport ratio over its maximum possible value. Two different modelling results are shown depending on whether the ED system is dealing with brackish water or a high salinity source. The equations that relate the mass transfer units (MTU), the concentration ratio (CR), and the resistance ratio (ER) to other system parameters such as effectiveness are developed. Finally, the model is tested by comparing its results to both salinity levels. The errors found are ~ 0.02 % for the brackish water source (3500 ppm) and ~ 2 % for the high salinity source (150,000 ppm). Therefore, the ε -MTU model developed can help to design and evaluate ED systems in a robust manner.

3.1. Introduction

Electrodialysis (ED) is an important technique in desalination, particularly in the treatment of brackish and seawater [6], [58]. It possesses various advantages and has gained recognition as a practical and efficient desalination technology [59–61]. ED is a membrane separation method that uses charged membranes and electrical potential difference to separate ions from an aqueous solution [62], [63]. A set of stacks are combined to form the ED system. In every stack, there is an anode and a cathode (to apply the direct current potential). The ED stack also consists of compartments of electrode rinse at the cells nearby the cathode and the anode. The membranes used in the ED system are positively charged membranes (anion exchange membranes, AEM), and negatively charged membranes (cation exchange membranes, CEM). These alternatively arranged charged ionic membranes (AEM and CEM) are placed this way in the stack to manage the transfer of salt ions between the compartments. CEM allows the transfer of the cations from dilute side to the concentrate side, and the next AEM membrane will prevent the transfer of these ions since they have the same charge. In the same way, the AEM will allow the transfer of the anions from dilute side to the concentrate side, and CEM will prevent these ions of the same sign from transferring through it. By this process, the salt will be decreased from the dilute compartment since it

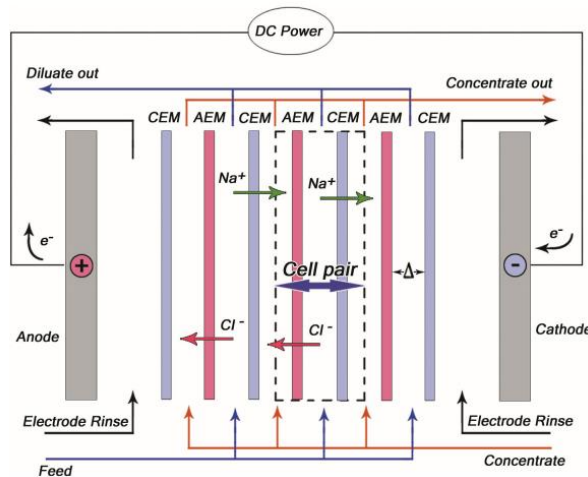


Figure 3-1. Electrodialysis stack schematic desalination diagram [1]

transferred to the concentrate side, which leads to producing freshwater and is obtained at the dilute compartment outlet as shown in Fig. 3-1. Having a CEM membrane, an AEM membrane, a concentrate compartment, and a dilute compartment constitutes what is called a cell pair in the ED stack.

To determine the ED system performance, each of its process parameters is considered such as the concentration of the compartments, the permselectivity of the membranes, current density, the velocities of the flow in the compartments, and recovery rates [64]. These parameters vary according to the application in which ED is used. Many experimental and mathematical methods were taken for optimizing and analysing ED systems [65–68]. Several models were considered to analyse the performance of the system, some of which are simple. They are used for brackish water treatment in low concentrations systems [10], [69–71]. The others are more detailed and complicated for accuracy in higher salinity treatment.

A lumped model was introduced by Lee et al. for designing Brackish water ED systems [69]. It is the simplest model since it ignored the boundary film effect due to polarization that occurs by salt ion accumulation close to the charged membranes. It also ignores the water that is passing through the membranes due to osmosis and electro-osmosis, referred to as water transport. Tsiakis and Papageorgiou [70] implemented the model of Lee et al. for each stack independently aimed at determining a detailed design of the multi-stage ED system. The study optimized the construction of an ED stack, while determining stages, cell-pairs, voltage, current, current density, and feed parameters. Furthermore, the model minimized the total cost of the ED plant. Since ED is a membrane separation process, concentration polarization is one of the challenges that must be considered in modelling the system. Concentration polarization (CP) in ED results from ion transport differences, causing concentration gradients on the membrane surfaces and leading to limited ion current density and possible salt precipitation [10]. CP alters ion mobility, resulting in lower conductivity near the dilute side of the membrane and greater conductivity towards the

concentrate side. Equivalent conductivity is crucial in ED for efficient ion transport through membranes, influencing separation efficiency and overall system performance [71], [72]. Qureshi and Zubair [71] found that varying the equivalent conductivity does not have a significant practical effect for typical brackish water feed concentrations. This supports the assumption of taking the dilute bulk electrical conductivity as a constant and same, ignoring its variation with concentration. The Donnan potential is the voltage difference across a membrane caused by uneven ion distribution [73]. It is an important concept in electrodialysis since it influences the unit cell voltage by considering the ion distribution across membranes [6], [74–77]. Qasem et al. [78] introduced the Donnan potential to the lumped model, showing that this significantly reduced the error in specific energy consumption prediction. Furthermore, the difference between the size prediction of both models increased with higher feed to product salinity difference. Water transport that is a result of osmosis and electro-osmosis was neglected. Water transport in ED is an important effect that impacts system performance, membrane fouling, and overall efficiency [79], [80]. To further enhance the Lee et al. lumped model, more thermodynamic potentials were included such as boundary layer films and water transport [1]. This enhanced the accuracy of the model, which allowed dealing with a high range of feed salinities. It should be noted that water transport effect should be considered at salinities which are more than 50 ppt [81–84].

In heat exchangers, there are two fluids flowing that are different in temperature as shown in Fig. 3-2(a). It has hot fluid flowing in one channel and cold fluid flowing in the other. The differential heat transfer is a result of the temperature difference (the driving force) between the hot and cold fluid. The reciprocal of the overall heat transfer coefficient (U_{th}) represents the resistance of the heat flow per unit area [85]. A similar schematic drawing can be made for an ED system that shows a mass exchanger analogous to the heat exchanger (See Fig. 3-2(b)). A feed with high salinity enters from the inlet of the concentrate compartment of the mass exchanger, and another lower salinity feed enters from the inlet of the dilute compartment. Since the salt solution has charged ions, the electric field moves them from the concentrate side to the dilute side through the ion-

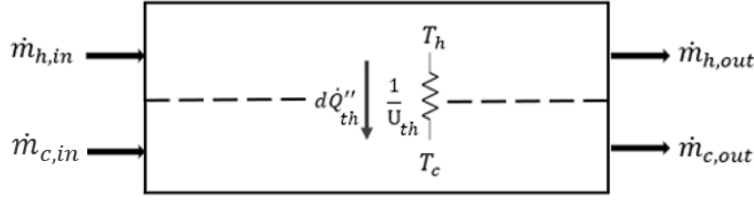


Figure 3-2(a). Schematic drawings of Heat exchanger with two inlet streams

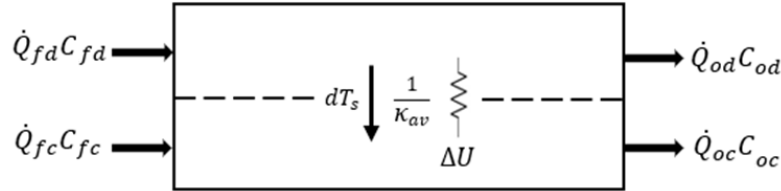


Figure 3-2(b). Schematic drawings of ED mass exchanger with two inlet streams

permeable membranes. This will result in producing more diluted water with less salinity in the outlet of the dilute compartment. Each ED stack is under an electrical potential difference (U) as the driving force, and the specific electrical conductivity is κ_{av} .

The effectiveness-Number of Transfer Units (ε -NTU) methods, developed by Kays and London [86], is used in heat exchanger design, which helps in evaluating their performance [87]. This method has the effectiveness, the NTU, and the heat capacity rate ratio as three groups that are dimensionless and used in the model. The effectiveness is the ratio of the actual heat transferred to the maximum possible heat transfer. The NTU combines several parameters, i.e. transfer area, the overall heat transfer coefficient, heat capacity, and fluid flow rate [54]. The heat capacity rate ratio is the ratio of minimum to the maximum thermal capacitance among the two streams. Many efforts have been made over the last few decades to build dimensionless correlations between performance and the number of transfer units for both heat and mass transfer. With these dimensionless correlations, ε -NTU can be used to estimate and design system parameters [87–91].

The effectiveness-Mass Transfer Unit method (ε -MTU) in ED is analogous to the ε -NTU concept in heat transfer [92]. It quantifies mass transfer efficiency in ED the same way that NTU quantifies heat transfer efficiency. Both approaches provide a method for evaluating and optimizing the

effectiveness of mass or heat transfer mechanisms. In this chapter, a series of analytical equations are derived to develop an ε -MTU method for ED mass exchangers. Some nondimensional parameters are defined and used as a tool to make the differential permeate flow rate equation as a nondimensional equation which is solved to give a closed-form expression. This reached expression helps in connecting the input condition of the operation to the effective size and the performance of the ED system. Several plots are done for the reached nondimensional form, and the ε -MTU method is tested on some ED plants to validate the work and to show the use of the method in designing the system.

3.2. Electrodialysis mass exchanger model

Fig. 3-3 shows a 2-D schematic drawing for an ED mass exchanger. Both channels have feed inlets to allow the flow of solutions with different salinities. As a result of the applied potential difference, the salt ions in the solution on the dilute side transports to the concentrate side as the fluid flows in the channel. The product is collected in the outlet of the dilute side, while the brine is collected on the concentrate side outlet. The conductivity and membrane area are also important parameters affecting the system results. The following assumptions are taken for the model:

1. The distances between the membranes are equal.
2. Feed flow rates of the dilute and the concentrate sides are the same ($\dot{Q}_{fd} = \dot{Q}_{fc} = \dot{Q}_f$).
3. The flow direction of the channels is parallel.
4. The current density is always below the limiting current density.
5. For the solution streams, the solution activity coefficient is taken as unity.
6. The membrane thickness is neglected.

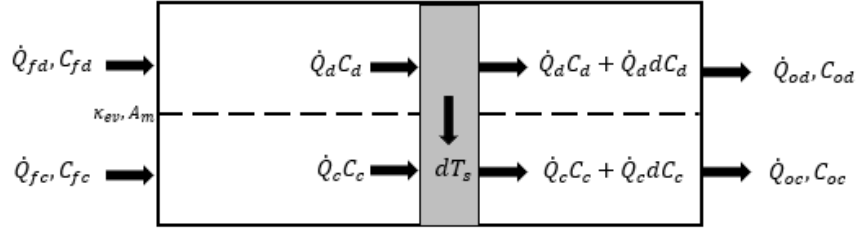


Figure 3-3. Schematic drawing of an ED mass exchanger

There are two situations that are considered for the ED mass exchanger model, which are the model with or without an additional assumption of neglecting the water transport that is passing through the membranes due to osmosis and electro-osmosis.

3.2.1. Mathematical model for ED brackish water (Neglecting water transport)

The current density is shown in the following equation [69]:

$$i = \frac{\kappa_{av} U_{tot}}{2\Delta N_{cp}} \quad (3.1)$$

where U_{tot} is the total applied potential on the stack (V), κ_{av} is the cell pair specific electrical conductivity (S/m), Δ is the compartment (channel) thickness (m) and N_{cp} is the number of cell pairs in a stack.

The differential salt transport from the dilute side to the concentrate side can be expressed as:

$$dT_s = \dot{Q}_f dC_s^\Delta = \frac{i\zeta N_{cp}}{zF\beta} dA \quad (3.2)$$

where T_s is the salt transport rate from the dilute side to the concentrate side (mol/s), $\dot{Q}_f$ is the inlet (feed) flow rate (m^3/s), C_s^Δ is the amount of salinity (mol/m^3), F is the Faraday constant ($A.s/mol$), ζ is the factor related to current utilization, z is valence ($z = 1$ for NaCl) and β is the shadow factor.

Substitution of Eq. (3.1) into Eq. (3.2) yields:

$$dT_s = \dot{Q}_f dC_s^\Delta = \frac{\zeta \kappa_{av} U_{tot}}{2\Delta z F \beta} dA \quad (3.3)$$

The salt transport is also defined as the difference between the dilute feed salinity and the fluid salinity at a point in the stream, which is equal to the difference between a point in the stream and the concentrate feed salinity. Since the water transport is neglected, the water flow rate will remain constant and, therefore, we may write:

$$C_s^\Delta = C_{fd} - C_d = C_c - C_{fc} \quad (3.4)$$

The cell pair specific electrical conductivity is given by:

$$\kappa_{av} = \frac{2\Delta}{\left[\frac{\Delta}{\kappa_c} + \frac{\Delta}{\kappa_d} + r_m + r_{don} \right]} \quad (3.5)$$

The electrical conductivities, κ_c and κ_d , are expressed by the equivalent conductance and concentrations as:

$$\kappa_c = \Lambda C_c \quad (3.6)$$

$$\kappa_d = \Lambda C_d \quad (3.7)$$

The total area resistance is a summation of the boundary layer, the membranes, and the Donnan potential resistances. i.e.

$$r_{tot} = r_m + r_{don} \quad (3.8)$$

Now, the required dimensionless quantities will be defined:

The transport ratio (TR) is the ratio of the amount of salt transported to the feed salinity of the dilute stream. It shows the amount of salt removed from the water in terms of a fraction.

$$TR = \frac{C_s^\Delta}{C_{fd}} \quad (3.9)$$

The concentration ratio (CR) is the feed salinity of the dilute side divided by the feed salinity of the concentrate side.

$$CR = \frac{C_{fd}}{C_{fc}} \quad (3.10)$$

The resistance ratio (ER) is represented by the dilute feed concentration, the total area resistance, the equivalent conductivity, and the cell chamber thickness as follows:

$$ER = \frac{C_{fd}}{\Delta/\Lambda r_{tot}} \quad (3.11)$$

The number of transfer units (NTU) of the heat exchanger is used to make an analogy to the dimensionless parameter MTU for ED mass exchangers. The MTU is found to be (See the Appendix for derivation):

$$MTU = \frac{\zeta \Lambda U_{tot} A}{\Delta z F \dot{Q}_f} \quad (3.12)$$

Now, the salt transport equation (3.2) can be expressed with the pair specific electrical conductivity equation (3.5) as:

$$dT_s = \dot{Q}_f dC_s^\Delta = \frac{\zeta U_{tot}}{zF\beta \left[\frac{\Delta}{\kappa_c} + \frac{\Delta}{\kappa_d} + r_m + r_{don} \right]} dA \quad (3.13)$$

Applying the definitions in Eqs. (3.6-3.8), we get

$$\dot{Q}_f dC_s^\Delta = \frac{\zeta U_{tot}}{zF\beta \left[\frac{\Delta}{\Lambda C_c} + \frac{\Delta}{\Lambda C_d} + r_{tot} \right]} dA \quad (3.14)$$

By dividing both sides by the feed salinity of the dilute side (C_{fd}), substituting the salt balances from Eq. (3.4), applying the non-dimensional equations Eqs. (3.9-3.12), and then adjusting the equation, Eq. (3.14) results in:

$$dMTU = \left(\frac{1}{CR^{-1} + TR} + \frac{1}{1 - TR} + ER \right) dTR \quad (3.15)$$

The boundary condition is that, at the inlet, the mass transfer unit, $MTU = 0$ at transport ratio $TR = 0$ and $MTU = MTU$ at transport ratio $TR = TR$. The result of integrating Eq. (3.15) gives:

$$MTU = ER \times TR + \ln \left(\frac{1 + TR \times CR}{1 - TR} \right) \quad (3.16)$$

This relation (3.16) helps in designing the membrane of ED mass exchanger by determining the effective surface area of the membrane using the required mass transfer units. Figs. 3-4(a-d) show the relation of the transport ratio (TR) with the mass transfer units (MTU) at different concentration ratios (CR) and resistance ratios (ER).

Fig. 3-4(a) shows that increasing the resistance ratio has a notable impact on the required MTU value for a given TR. When the resistance ratio is higher or the permeate feed salinity increases, the MTU value needed to achieve the desired transport ratio increases significantly.

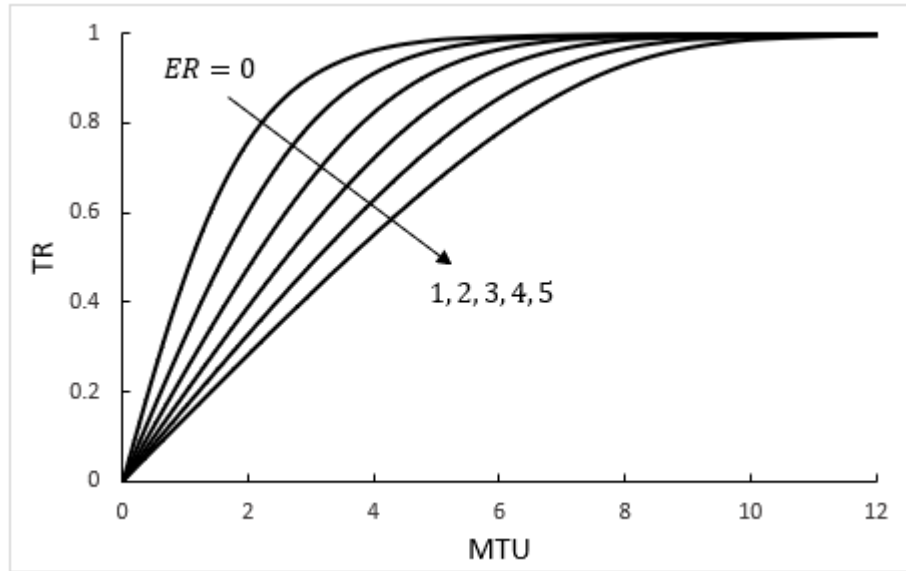


Figure 3-4(a). Transport ratio vs mass transfer units at different resistance ratio (ER) when $CR = 0.1$

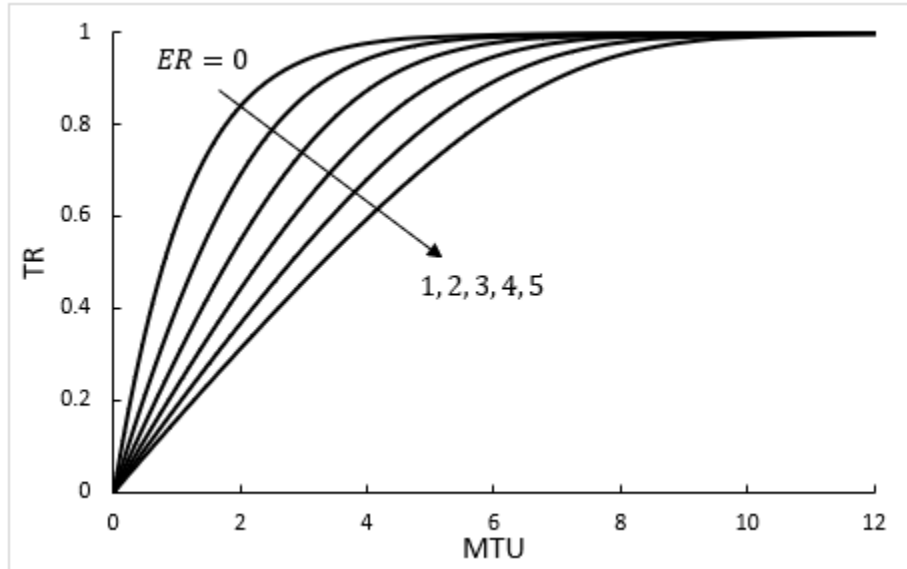


Figure 3-4(b). Transport ratio vs mass transfer units at different resistance ratio (ER) when $CR = 0.4$

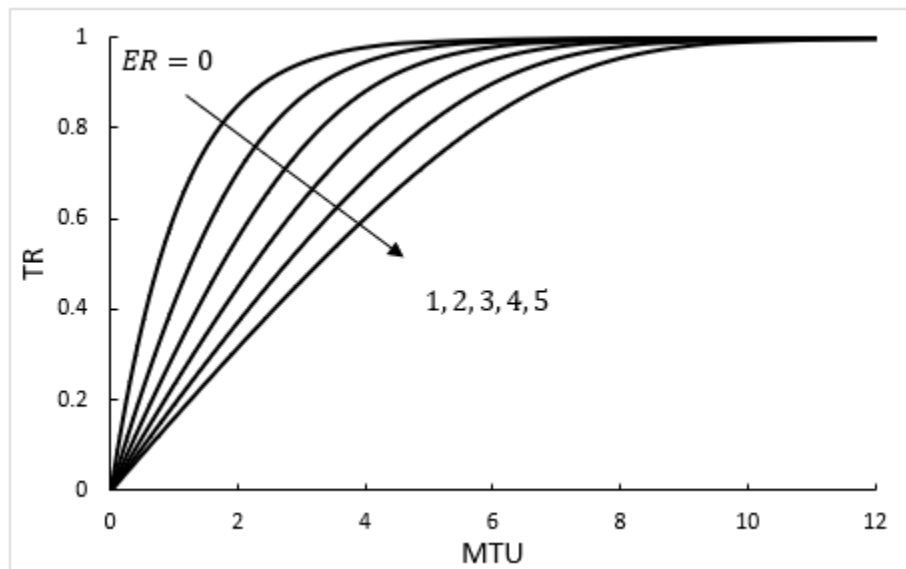


Figure 3-4(c). Transport ratio vs mass transfer units at different resistance ratio (ER) when $CR = 0.7$

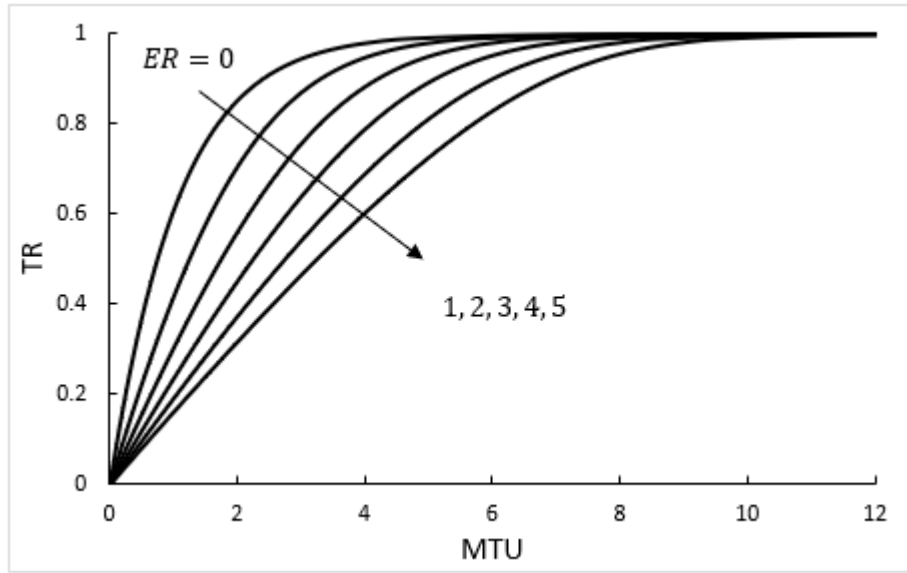


Figure 3-4(d). Transport ratio vs mass transfer units at different resistance ratio (ER) when CR = 0.9

Also, Figs. 3-4 (b-d) show that, as CR increases, the corresponding MTU value for a specific transport ratio also increases. This means that a higher CR requires a larger MTU to achieve the desired ion removal efficiency. This emphasizes the importance of considering the total resistance and the concentration difference between the feeds in the design of an ED mass exchanger.

Now, the concentration factor (CF) is a parameter used to identify the concentration degree reached by the process. It is the ratio of the exiting salinity in a stream to the salinity of the feed entering the stream. Using the salt balance, Eq. (3.4), and the introduced non-dimensional terms, Eqs. (3.9)-(3.10),

For the dilute side:

$$CF_d = \frac{C_{od}}{C_{fd}} = 1 - TR \quad (3.17)$$

For the concentrate side:

$$CF_c = \frac{C_{oc}}{C_{fc}} = 1 + CR \times TR \quad (3.18)$$

Sometimes the designer is limited to a certain brine salinity value, which makes the concentration factor important to consider by relating it to the maximum MTU allowable. Fig. 3-5 shows the concentration factor for both streams as a function of the mass transfer units at $CR = 0.7$ and different ER values. Fig. 3-6 shows a relation between the brine concentration of a brackish water feed inlet salinity of 3.5 g/kg at $CR = 0.1, 0.7$. The concentration ratio depends on the application that ED is used for. Therefore, its value must be considered as well. If CR is close to one, the salinity of the brine will be less than in the case of a small value of CR , as shown in Figs 3-6(a, b). It can be noted that all these design parameters can be obtained by simply determining the MTU value associated with a certain TR value.

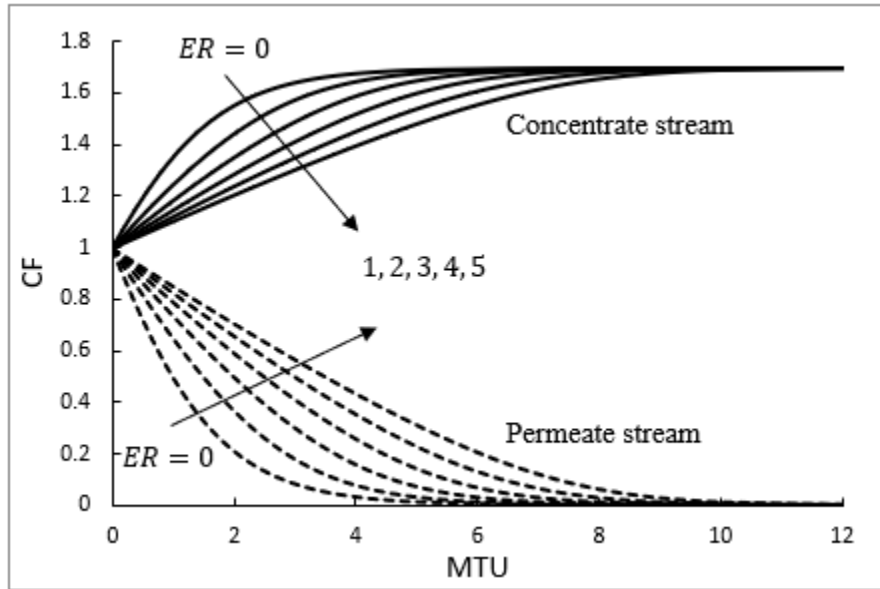


Figure 3-5. The concentration factor vs the mass transfer units at different resistance ratios and $CR = 0.8$

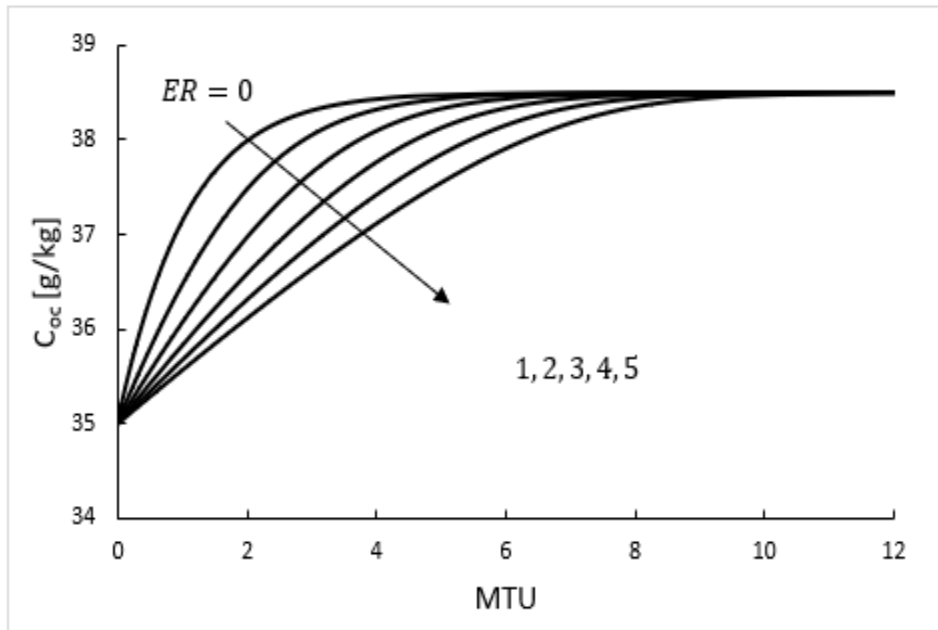


Figure 3-6(a). Brine salinity vs Mass transfer units at different resistance ratios (ER) when $CR = 0.1$. The dilute channel inlet feed salinity is $C_{fd} = 35 \text{ g/kg}$

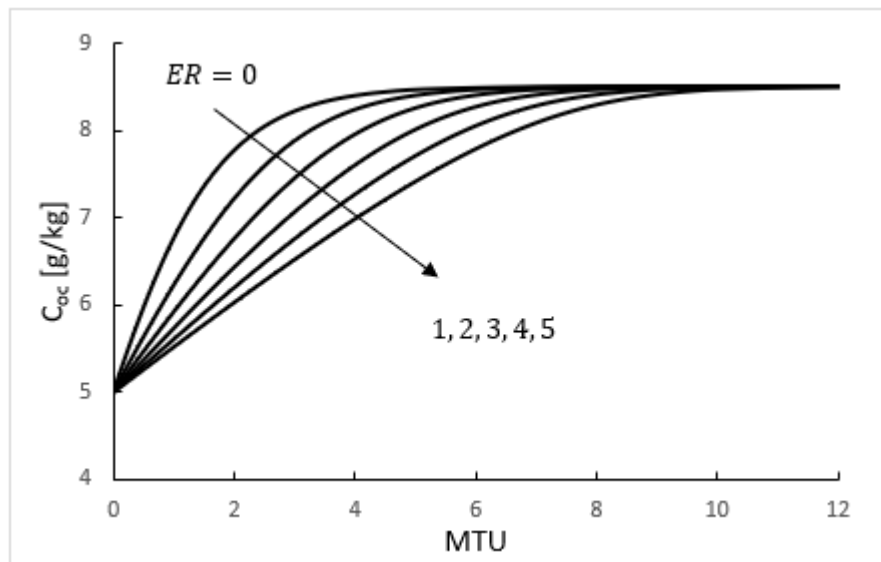


Figure 3-6(b). Brine salinity vs Mass transfer units at different resistance ratios (ER) when $CR = 0.7$. The dilute channel inlet feed salinity is $C_{fd} = 3.5 \text{ g/kg}$

3.2.2. Mathematical model for ED high saline water (Considering water transport)

As the feed flows along the channel, a portion of the water is transported with the salt through the membrane because of the osmosis and electro-osmosis effects. Therefore, the feed flow rate is changing along the channels (See Fig. 3-7).

The same equations are applied to the model, but with considering the change in the flow rate such that the salt transport is now defined as:

$$T_s = \dot{Q}_f C_s^\Delta = \dot{Q}_c C_c - \dot{Q}_f C_{fc} = \dot{Q}_f C_{fd} - \dot{Q}_d C_d \quad (3.19)$$

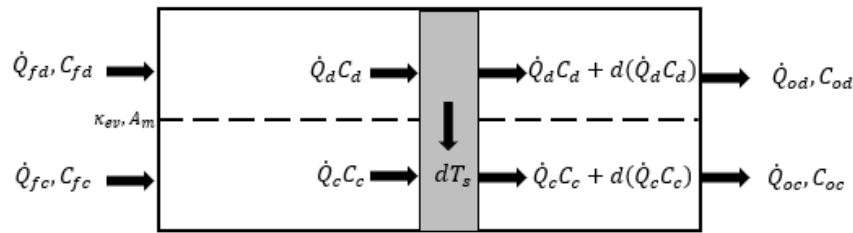


Figure 3-7. Schematic drawing of ED mass exchanger, considering water transport

Now, one more required dimensionless quantity is defined as the recovery ratio (RR), which is the fraction of the dilute flow rate to the feed flow rate.

$$RR = \frac{\dot{Q}_d}{\dot{Q}_f} \quad (3.20)$$

Using the recovery rate definition, Eq. (3.19) yields [1]:

$$T_s = \dot{Q}_f (C_{fd} - RRC_d) = \dot{Q}_f [(2 - RR)C_c - C_{fc}] \quad (3.21)$$

During the flow of high salinity water, solutes accumulate near the membrane causing concentration polarization, and therefore a thin layer of water, called boundary layer, forms. The total area resistance is a summation of the boundary layer, the membranes, and the Donnan potential resistances. i.e.

$$r_{tot} = r_{BL} + r_m + r_{don} \quad (3.22)$$

The cell pair specific electrical conductivity is given by [1]:

$$\kappa_{av} = \frac{2\Delta}{\left[\frac{\Delta - 2\delta}{\kappa_c} + \frac{\Delta - 2\delta}{\kappa_d} + r_{BL} + r_m + r_{don} \right]} \quad (3.23)$$

Where δ is the boundary film thickness. The new resistance ratio (ER_h) is represented by the dilute feed concentration, the total area resistance, the equivalent conductivity, the cell chamber thickness, and the boundary film thickness as follows:

$$ER = \frac{C_{fd}}{(\Delta - 2\delta)/\Lambda r_{tot}} \quad (3.24)$$

The number of transfer units (NTU) of the heat exchanger is used to make an analogy to the dimensionless parameter MTU for ED mass exchangers. The MTU is found to be (See the Appendix for derivation):

$$MTU = \frac{\zeta \Lambda U_{tot} A}{\dot{Q}_f (\Delta - 2\delta) zF} \quad (3.25)$$

The salt transport can be expressed with the pair specific electrical conductivity Eq. (3.23) with using the definitions Eqs. (3.6) – (3.7) and Eq. (3.22) as:

$$dT_s = \dot{Q}_f dC_s^\Delta = \frac{\zeta U_{tot}}{zF\beta \left[\frac{\Delta - 2\delta}{\Lambda C_c} + \frac{\Delta - 2\delta}{\Lambda C_d} + r_{tot} \right]} dA \quad (3.26)$$

By dividing both sides by the feed salinity of the dilute side (C_{fd}), substituting the salt balance Eq. (3.19), applying the non-dimensional equations, i.e. Eqs. (3.9), (3.10), (3.12), (3.20), and (3.24), then adjusting the result, Eq. (3.26) gives the following:

$$dMTU = \left[\frac{(2 - RR)}{CR^{-1} + TR} + \frac{RR}{1 - TR} + ER \right] dTR \quad (3.27)$$

The boundary condition is that, at the inlet, $MTU = 0$ at $TR = 0$ and $MTU = MTU$ at $TR = TR$. The result of the integration of Eq. (3.27) is:

$$MTU = TR \times ER + \ln \frac{(1 + CR \times TR)^{(2-RR)}}{(1 - TR)^{RR}} \quad (3.28)$$

This equation helps in designing the membrane of ED mass exchanger by determining the effective surface area of the membrane using the required mass transfer unit. Figs 3-8(a-d) show the relation of the transport ratio, with the mass transfer units at different resistance ratios and recovery ratios. Fig. 3-8(a) illustrates the variation at $RR = 1$ where it shows the exact result to the previous case that did not consider water transport effect in the model. Figs. 3-8(b-d) show that the MTU decreases as the recovery ratio is decreased. It is important to note that the recovery ratio should be balanced with the desired product salinity and system efficiency. Since lower recovery ratio may lead to a lower MTU value, it also means that a larger portion of the permeate flow rate is being wasted to the concentrate channel.

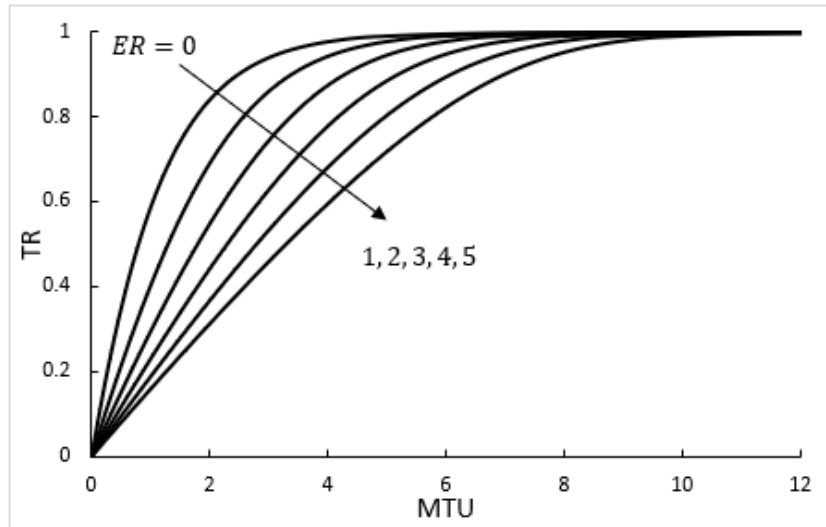


Figure 3-8(a). Transport ratio vs mass transfer units at different resistance ratio (ER) when $CR = 0.2$ and $RR = 1$

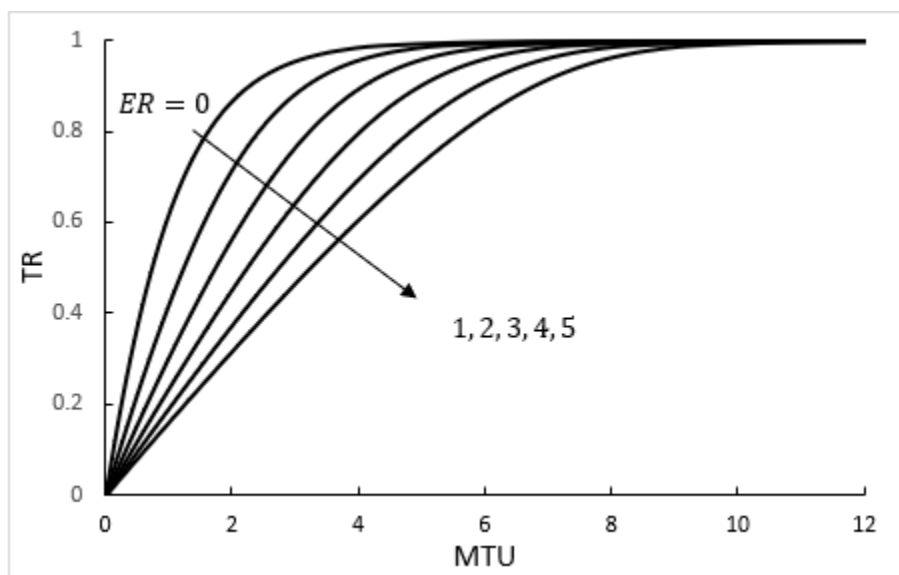


Figure 3-8(b). Transport ratio vs mass transfer units at different resistance ratio (ER) when $CR = 0.2$ and $RR = 0.9$

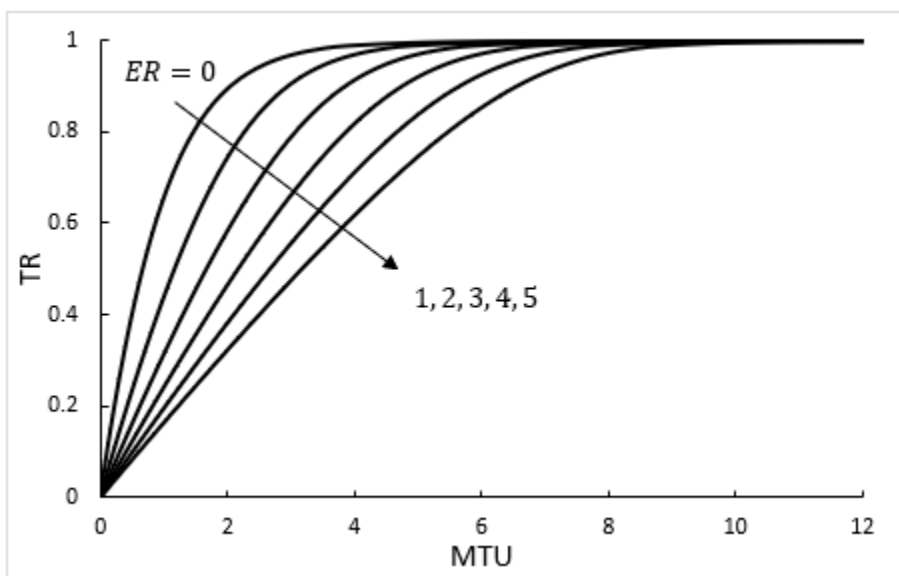


Figure 3-8(c). Transport ratio vs mass transfer units at different resistance ratio (ER) when $CR = 0.2$ and $RR = 0.8$

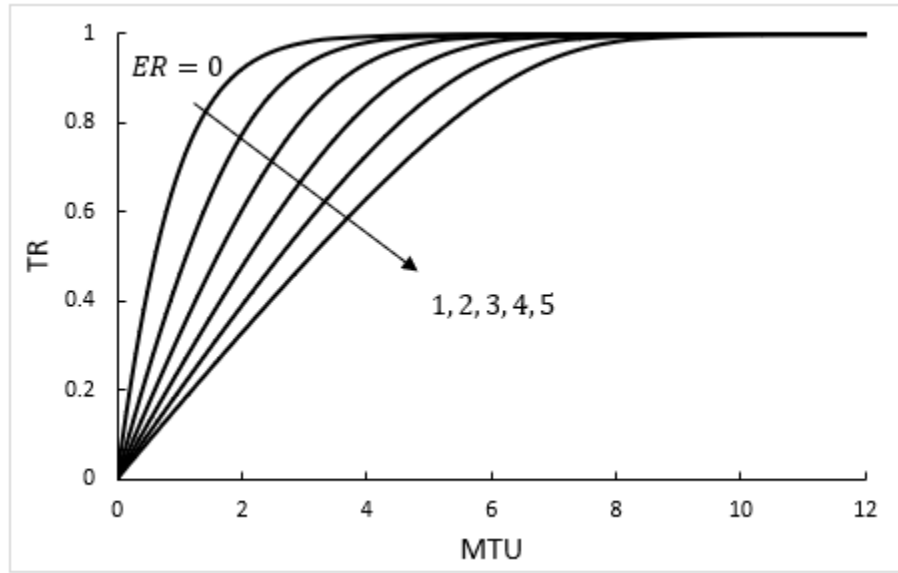


Figure 3-8(d). Transport ratio vs mass transfer units at different resistance ratio (ER) when CR = 0.2 and RR= 0.7

3.3. Electrodialysis parameters and relations with MTU

3.3.1 Concentrate stream salinity

Depending on the recovery ratio, the flow rates of the product and concentrate are not the same in ED. One flow stream must be operated in feed and bleed mode to maintain equivalent linear flow velocities in both dilute and concentrate cells [93]. This means that a portion of the feed solution is continuously bled off to keep the cell volume constant while maintaining the flow rate and velocity constant. This maintains the concentration gradient across the membrane, allowing for effective ion transport. So, the concentrations of both streams are related to the recovery rate as [69]:

$$C_c = \frac{C_{fd} - RRC_d}{1 - RR} \quad (3.29)$$

$$C_{fc} = \frac{C_{fd}(1 - RR)}{RR} + \frac{C_c(2RR - 1)}{RR} \quad (3.30)$$

Substituting Eq. (3.29) to Eq. (3.30):

$$C_{fc} = \frac{C_{fd}(1 - RR)^2 + (C_{fd} - RRC_d)(2RR - 1)}{RR(1 - RR)} \quad (3.31)$$

3.3.2. The current density and the limiting current density

After finding the mass transfer unit parameter, it can also be expressed in a variety of ways based on the given input parameters required to operate the system. Applying Eq. (3.1) - Eq. (3.12) yields:

$$MTU = \frac{2\Delta N_{cp}\zeta\Lambda iA}{\kappa_{av}\Delta zF\dot{Q}_f} \quad (3.32)$$

The limiting current density in ED refers to the highest current density that can be applied to the membrane without causing damage or a significant drop in performance [94]. When the electric field strength is high enough to cause physical and chemical changes in the membrane, such as electrolysis, deterioration, or fouling, this limit is achieved. To avoid reaching the limiting current density, the applied voltage and current must be carefully managed and modified based on the membrane and feed solution parameters [69], [95], [96].

$$i = si_{lim} = sx C_d u^y \quad (3.33)$$

where s is the safety factor, which is the fraction of the limiting current density that represents the actual operating current density, and x and y are empirical constants. By substituting Eq. (3.33) into Eq. (3.32):

$$MTU = \frac{2\Delta N_{cp}\zeta\Lambda si_{lim}A}{\kappa_{av}\Delta zF\dot{Q}_f} \quad (3.34)$$

$$MTU = \frac{2\Delta N_{cp}\zeta\Lambda sxC_d u^y A}{\kappa_{av}\Delta zF\dot{Q}_f} \quad (3.35)$$

3.3.3. The shadow effect

The presence of a spacer can have a considerable impact on the distribution of current within the cell. This is because the spacer creates a shadow effect, making some sections of the membrane inaccessible to current and resulting in an uneven current density [97]. Thus, a higher membrane area than the anticipated applicable membrane area is required to address this phenomenon [98]. This guarantees that there is enough membrane surface accessible to accept the appropriate current and achieve the desired degree of performance [69]. Therefore,

$$A_{prac} = \frac{A_{eff}}{\beta} \quad (3.36)$$

where β is the shadow factor that accounts for the shadow effect. Including Eq. (3.36) to the MTU parameter gives:

$$MTU = \frac{\zeta\Lambda U_{tot}\beta A_{prac}}{\Delta zF\dot{Q}_f} \quad (3.37)$$

Or,

$$MTU = \frac{2\Delta N_{cp}\zeta\Lambda sxC_d u^y \beta A_{prac}}{\kappa_{av}\Delta zF\dot{Q}_f} \quad (3.38)$$

3.3.4. The practical length

The practice length is an important parameter in designing the ED mass exchanger. It refers to the total length of the flow channel from the feed input to the product output. It is an important consideration when evaluating the number of stacks needed in an ED system to achieve the desired product purity and concentration.

$$A_{prac} = w L_{prac} \quad (3.39)$$

where w is the effective width of the cell. Also,

$$L_{prac} = N_{st}L_{st} \quad (3.40)$$

where L_{st} is the length of a stack and N_{st} is the total number of stacks in series. Substituting Eq. (3.39) into Eqs. (3.38) and (3.28) leads to:

$$MTU = \frac{\zeta \Lambda U_{tot} \beta w L_{prac}}{\Delta z F \dot{Q}_f} \quad (3.41)$$

Or,

$$MTU = \frac{2\Delta N_{cp} \zeta \Lambda s x C_d u^y \beta w L_{prac}}{\kappa_{av} \Delta z F \dot{Q}_f} \quad (3.42)$$

3.3.5. The practical flow rate

The presence of these spacers, on the other hand, lowers the volume available for solution flow, resulting in higher flow velocity. As a result, the practical flow rate can be stated as follows:

$$\dot{Q}_f = \frac{N_{cp} A_{prac} \Delta u \alpha}{L_{prac}} = N_{cp} w \Delta u \alpha \quad (3.43)$$

Table 3-1 summarizes all the MTU relations.

Table 3-1. MTU relations with different ED parameters.

ED parameter	MTU
Applied voltage	$\frac{\zeta \Lambda U_{tot} A}{\Delta z F \dot{Q}_f}$
current density	$\frac{2 \Delta N_{cp} \zeta \Lambda i A}{\kappa_{av} \Delta z F \dot{Q}_f}$
Limiting current density	$\frac{2 \Delta N_{cp} \zeta \Lambda s i_{lim} A}{\kappa_{av} \Delta z F \dot{Q}_f}$
	$\frac{2 \Delta N_{cp} \zeta \Lambda s x C_d u^y A}{\kappa_{av} \Delta z F \dot{Q}_f}$
Practical area	$\frac{\zeta \Lambda U_{tot} \beta A_{prac}}{\Delta z F \dot{Q}_f}$
	$\frac{2 \Delta N_{cp} \zeta \Lambda s x C_d u^y \beta A_{prac}}{\kappa_{av} \Delta z F \dot{Q}_f}$
Practical Length	$\frac{\zeta \Lambda U_{tot} \beta w L_{prac}}{\Delta z F \dot{Q}_f}$
	$\frac{2 \Delta N_{cp} \zeta \Lambda s x C_d u^y \beta w L_{prac}}{\kappa_{av} \Delta z F \dot{Q}_f}$

3.4. Electrodialysis effectiveness (ε -MTU model)

The effectiveness of an ED system can be defined as the ratio of the actual amount of the transported salt by a certain size of the mass exchanger to the maximum possible salt transport.

$$\varepsilon = \frac{\text{actual salt transport from the dilute side}}{\text{maximum salt transport from the dilute side}} \quad (3.44)$$

From Eq. (3.19), and with considering the minimum reached product salinity as zero, the effectiveness equation can be expressed as (Also called the system “chemical efficiency” [99]):

$$\varepsilon = \frac{T_{s,real}}{T_{s,max}} = \frac{\dot{Q}_f C_{fd} - \dot{Q}_d C_d}{\dot{Q}_f C_{fd} - \dot{Q}_d C_{d,min}} = 1 - RR \frac{C_d}{C_{fd}} \quad (3.45)$$

Also, using Eq. (3.19), the definition of the effectiveness can also be expressed considering the concentrate stream as (**Note:** $C_{c,max} = C_{fd} + C_{fc}$):

$$\varepsilon = \frac{T_{s,real}}{T_{s,max}} = \frac{\dot{Q}_f [(2 - RR)C_c - C_{fc}]}{\dot{Q}_f C_{c,max} - \dot{Q}_f C_{fc}} = \frac{(2 - RR)C_c - C_{fc}}{C_{fd}} \quad (3.46)$$

Equations (3.44) - (3.45) can be used to find the salinity of each stream at any arbitrary point as a function of the effectiveness.

$$C_d = \frac{C_{fd}(1 - \varepsilon)}{RR} \quad (3.47)$$

$$C_c = \frac{\varepsilon * C_{fd} + C_{fc}}{2 - RR} \quad (3.48)$$

By substituting Eqs. (3.47) - (3.48) and the non-dimensional parameters into Eq. (3.28), the effectiveness as a function of the MTU is found to be:

$$MTU = \varepsilon \times ER + \ln \frac{(1 + CR \times \varepsilon)^{(2-RR)}}{(1 - \varepsilon)^{RR}} \quad (3.49)$$

This can also be recognized from Fig. 3-4 and Fig. 3-8, where the effectiveness is the actual transport ratio (TR) of the ED mass exchanger system to the maximum possible transport ratio (TR_{max}). These TR vs MTU figures show that the maximum possible transport ratio goes to one i.e. $\varepsilon \approx 1$ at $TR \approx 1$ (See Eq. (3.49)). It should also be noted that the maximum effectiveness requires a high MTU value.

$$\varepsilon = \frac{TR}{TR_{max}} = TR \quad (3.50)$$

Substituting Eq. (3.50) into Eq. (3.28) also leads to Eq. (3.49). Fig. 3-9 shows the variation of the effectiveness with the mass transfer units at various resistance ratios (ER), and recovery ratios (RR). Fig. 3-9(a) shows the variation in case where the water transport is neglected, while Fig. 3-9(b) includes the effect. Although it is theoretically possible to achieve a 100% salt removal rate in ED [100], several practical factors such as concentration polarization, membrane fouling, and membrane selectivity make it challenging. Moreover, the salt removal rate depends on the type and concentration of salt ions in the feed solution, with monovalent ions being easier to remove than divalent ions. Commercial ED systems typically achieve salt rejection rates ranging from 90% to 99%, depending on the specific operating conditions and the properties of the membranes used [1], [69], [101]. It should be noted that to obtain the required level of ion removal efficiency, energy efficiency and product quality, it is important to adjust the ED operating conditions and parameters.

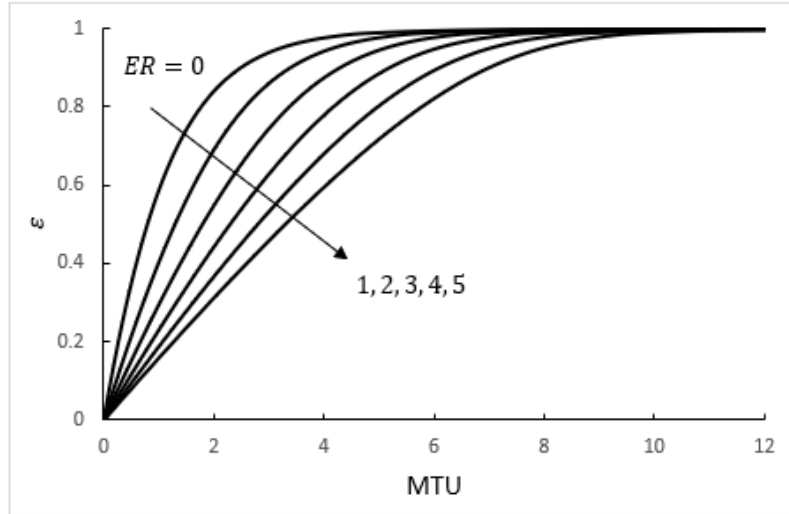


Figure 3-9(a). The effectiveness vs mass transfer units at different resistance ratio (ER) when $CR = 0.2$ and $RR = 1$

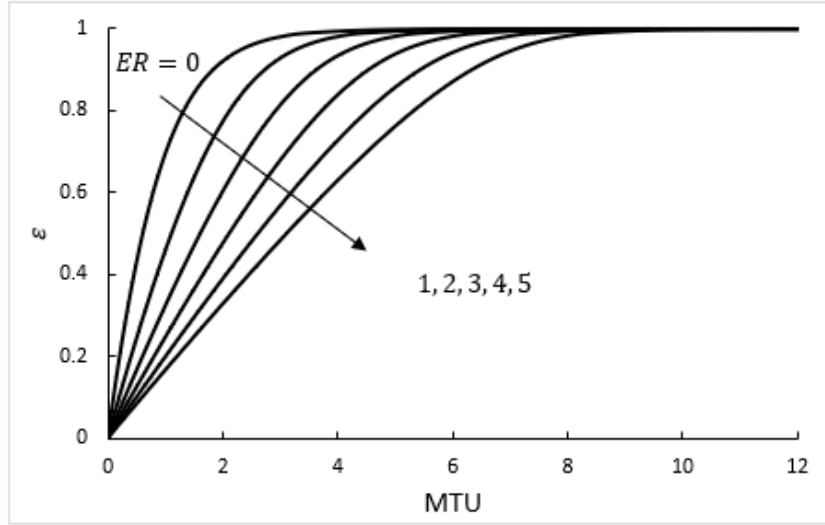


Figure 3-9(b). The effectiveness vs mass transfer units at different resistance ratio (ER) when CR = 0.2 and RR= 0.7

In ED, the electric field and the high concentration gradient are applied across the membranes to make the transport of salt ions from the product stream to the concentrate solution. The transport rate of salt is inversely proportional to the total resistance of the system while being directly proportional to the electric field strength and the concentration gradient. In other words, the lower concentration ratio (CR) and resistance ratio (ER), the better and higher transport ratio (TR) and effectiveness. It is also noted that:

$$C_{fc} \rightarrow \infty, \quad CR \rightarrow \frac{C_{fd}}{\infty} \rightarrow 0 \quad (3.48)$$

$$i_{lim} \rightarrow \infty, r_{tot} \rightarrow 0, \quad ER \rightarrow 0 \quad (3.49)$$

Applying Eqs. (3.48) – (3.49) to Eq. (3.24) at $RR = 1$ yields:

$$\varepsilon = 1 - e^{-MTU} \quad (3.50)$$

This equation shows an analogy to the heat exchanger effectiveness equation as the maximum heat capacity approaches infinity [54].

$$\varepsilon = 1 - e^{-NTU} \quad (3.51)$$

3.5. Design Examples

3.5.1. Designing an ED brackish water plant and neglecting water transport

Lee et al. [69] designed an ED plant intended to desalt brackish water with a total salinity of 3500 mg/l ($\sim 0.05833 \text{ keq/m}^3$) down to a diluate outlet concentration of 350 mg/l ($\sim 0.005833 \text{ keq/m}^3$). The objective is to find the total practical membrane area needed to reach this salinity while producing a total permeates flow rate of $350 \text{ m}^3/\text{d}$. Water transport through the membranes is neglected. The input data is given in Table 3-2.

Table 3-2. Input data for electrodialysis desalination plant design

Parameter	Symbol	Value
Recovery rate	RR	0.75
Equivalent solution conductance	Λ	$10.5 \text{ Sm}^2/\text{keq}$
Thickness of cell chamber	Δ	0.00065 m
Linear flow velocity	u	0.075 m/s
Constant a	x	$25,000 \text{ As}^b \text{ m}^{1-b} / \text{keq}$
Constant b	y	0.5
Faraday constant	F	$9.65 \times 10^8 \text{ As/keq}$
Volume factor	α	0.8
Shadow factor	β	0.7
Total membrane resistance	r_{tot}	$0.00076 \Omega \text{m}^2$
Safety factor	s	0.7
Current utilization factor	ζ	0.9

Effective cell width	w	0.42 m
Effective length of flow path per stack	L_{st}	0.725 m

Solution using the model:

Using Eqs. (3.29) - (3.30), the feed and outlet salinities of the concentrate stream are, respectively:

$$C_{fc} = 0.16333\text{ keq/m}^3, \quad C_c = 0.21583\text{ keq/m}^3$$

The non-dimensional parameters are calculated as:

$$TR = \frac{C_s^\Delta}{C_{fd}} = \frac{0.0525}{0.05833} = 0.9$$

$$CR = \frac{C_{fd}}{C_{fc}} = \frac{0.05833}{0.16333} = 0.357$$

$$ER = \frac{C_{fd}}{\Delta/\Lambda r_{tot}} = \frac{0.05833}{0.00065/(10.5 \times 0.0007)} = 0.6596$$

Fig. 3-4 or Eq. (3.16) is used to find the MTU value.

$$MTU = 3.175$$

This MTU value enables us to obtain the area using Eq. (3.38),

$$A_{prac} = 1.521\text{ m}^2$$

The number of cells can be found using Eq. (3.43):

$$N_{cp} = \frac{\dot{Q}_f}{w\Delta u\alpha} = 247.31 \approx 247\text{ cells}$$

So, the total area using the ε -MTU model will be $A_{tot} = 2N_{cp}A_{prac} = 752.18\text{ m}^2$. Lee et al. [69] found the total area as 752.343 m^2 resulting in an error of only 0.022%. Note that the practical

length and the applied voltage can also be found from the MTU value using the relations in Table 3-1 such that:

$$L_{prac} = 3.621 \text{ m} \quad ; \quad U_{tot} = 80.19 \text{ V}$$

Also, the number of stacks can be found using Eqs. (3.36) as:

$$N_{st} = L_{prac}/L_{st} = 4.994 \approx 5 \text{ stacks}$$

3.5.2. Designing ED high salinity water plant with water transport

Qasem et al. [1] designed an ED plant intended to desalt brackish water with a total salinity of 150000 *ppm* down to a diluate outlet concentration of 350 *ppm*. The objective is to find the total practical membrane area needed to reach this salinity while producing a total permeate flow rate of 350 m^3/d . Water transport through the membranes is considered. The input data is given in Table 3-3.

Table 3-3. Input data for electrodialysis desalination plant design

Parameter	Symbol	Value
Recovery rate	RR	0.48
Equivalent solution conductance	Λ	$10.5 \text{ Sm}^2/\text{keq}$
Thickness of cell chamber	Δ	0.00018 m
Boundary film thickness	δ	$1.152 \times 10^{-5} \text{ m}$
Linear flow velocity	u	0.1 m/s
Constant a	x	$25,000 \text{ As}^b \text{ m}^{1-b} / \text{keq}$
Constant b	y	0.5

Faraday constant	F	$9.65 \times 10^8 \text{ As/keq}$
Volume factor	α	0.8
Shadow factor	β	0.712
Total membrane resistance	r_{tot}	$0.0007 \Omega m^2$
Safety factor	s	0.5
Current utilization factor	ζ	0.9
Effective cell width	w	0.42 m
Effective length of flow path per stack	L_{st}	0.725 m

Solution using the model:

Using Eqs. (3.29) - (3.30), the feed and outlet salinities of the concentrate stream are, respectively:

$$C_{fc} = 138488 \text{ ppm}, \quad C_c = 288138 \text{ ppm}$$

The non-dimensional parameters are calculated as:

$$TR = \frac{C_s^\Delta}{C_{fd}} = \frac{150000 - 350}{150000} = 0.9977$$

$$CR = \frac{C_{fd}}{C_{fc}} = \frac{150000}{138488} = 1.1$$

$$ER = \frac{C_{fd}}{(\Delta - 2\delta)/\Lambda r_{tot}} = \frac{150000}{0.000157 / \left(\frac{10.5}{60 \times 1000} \times 0.00076 \right)} = 117.1$$

Eq. (3.28) is used to find the MTU value.

$$MTU = 120.8$$

This MTU value enables us to obtain the area using Eq. (3.25) and Eq. (3.36).

$$MTU = \frac{\zeta \Lambda U_{tot} \beta A_{prac}}{\dot{Q}_f (\Delta - 2\delta) zF}$$

$$A_{prac} = 19.59 \text{ m}^2$$

The number of cells can be found using Eq. (3.43)

$$N_{cp} = \frac{\dot{Q}_f}{w \Delta u \alpha} = 700 \text{ cells}$$

So, the total area using ε -MTU model will be $A_{tot} = 2N_{cp}A_{prac} = 26,236 \text{ m}^2$. Qasem et al. [1] found the total area as $25,760 \text{ m}^2$. The error between the ε -MTU result and the reference result is 1.85%.

3.6. Results and discussion

The MTU method is applied to an ED mass exchanger to analyze and optimize the process mass transfer efficiency. Calculating the MTU value leads to evaluating the effectiveness of ion transport through the ion-exchange membranes and designing the ED system by determining the required membrane area. The transport ratio, Eq. (3.16), of the model was developed to design brackish water ED plants. It specifically focuses on treating brackish water, which is characterized by relatively low salinity compared to seawater. The low salinity allows neglecting the water transport through the membranes, which helps to focus solely on the ion removal process. The model takes into account factors like feedwater salinity, desired product water quality, membrane selectivity and operational parameters to optimize the ED system for brackish water treatment. Fig. 3-4 shows the variation of the transport ratio of ions with MTU at different concentration ratios (CR) and resistance ratios (ER). It can be seen from Fig. 3-4(a) the effect of ER on MTU values. Higher resistance can impede the movement of ions and result in lower mass transfer rates, leading to a higher value of MTU required for a specific ion removal ratio to be achieved. The

effect of ER ratio on MTU also illustrates the importance of the salinity of the feed of the permeate channel since high salinity gives a higher ER ratio that affects the needed MTU value. For example, if the system is designed to have a 0.9 transport ratio, it will have to have 2.4 mass transfer units at CR=0.1 and with an ideal transfer with zero resistance (i.e., ER=0), while it will need 6.9 mass transfer units at ER=5. The model also showed the effect of the concentration ratio (CR) to the transport ratio (TR). Figs. 3-4(b-d) showed that increasing the concentration ratio leads to a slight increase in the required MTU. So, CR value should also be considered and controlled since extremely high concentration ratios can lead to challenges such as increased osmotic pressure, membrane fouling, or concentration polarization, which can negatively impact the overall system performance. The determination of MTU value is useful for designing an electrodialysis system and determining the required membrane area that achieves the desired separation performance and effectiveness. The first design example showed the designing ED plant that deals with brackish water. The model succeeded in obtaining the area needed to obtain the required effectiveness (99.8%) of the system, with an error of 0.022%.

When an ED mass exchanger deals with high salinity treatments, the transport of water through the membrane becomes substantial and should be taken into account in system design and operation. Water molecules tend to move through the membrane with the ions in high-salinity solutions, which impacts the overall ion transport. Because water transport can induce changes in stream flow rate, it can impact the recovery ratio. If the product stream loses a lot of water due to water transport, the recovery ratio will be highly affected. It can be seen from the second design example that aims to design ED plant for high salinity source (150 ppt) that the recovery ratio is 48%, which is low due to the transport of water effect. The system design required a high area (26236 m^2) for reaching the required salinity, which requires more than 66 stacks. The error was found to be 1.85% compared with the reference [1]. The low errors observed in the design examples validate the accuracy and reliability of the ε -MTU model. By comparing the design results with the actual performance of the system and observing low errors, it confirms that the ε -

MTU model effectively predicts the ion removal process and the required system parameters. This validation also provides confidence in the model's ability to accurately estimate the number of required membrane stacks, the operating conditions, and other design considerations for low and high salinity sources. It can be seen that there is a slightly higher error in the design example for high salinity sources where water transport effect is considerable compared to examples with lower salinity (brackish water). The existence of water transport adds additional complexities to the electrodialysis process, which can impair the accuracy of design predictions. It is important to note that the ε -MTU model can still provide valuable insights and assistance for the design of electrodialysis systems for high salinity sources. Moreover, the transport ratio and the effectiveness are intimately related in the MTU concept. A higher transport ratio suggests a more efficient mass transfer process, which results in greater effectiveness. A lower transport ratio, on the other hand, refers to a less efficient mass transfer process, resulting in lower effectiveness.

3.7. Conclusion

A closed-form analytical solution for a one-dimensional ED mass exchanger is developed based on an analogy with heat exchangers. The system transport ratio varies with three introduced nondimensional groups, which are the mass transfer units, the concentration ratio, and the resistance ratio. The ε -MTU model is developed for ED systems that aims to treat brackish water or high salinity water, considering many system effects such as shadow effect and water transport. The model is applied to some designed plants and the results are compared. The error between the ε -MTU model and the designed plants is found to be from 0-3%.

Chapter 4

Hybrid Desalination Analysis through the Lens of the ϵ -MTU Model

Chapter Abstract:

On today's water treatment landscape, hybrid desalination systems are widely adopted due their effective outcomes. In this chapter, the effectiveness of hybrid desalination systems is explored using MTU analogy. The study delves into the combined use of Nanofiltration (NF) and Reverse Osmosis (RO) in two distinct configurations: first, a staged NF-RO integration for progressively purifying water; second, an NF-RO configuration focusing on brine treatment while obtaining permeate at each stage. Additionally, the research investigates the innovative combination of Electrodialysis (ED) and NF, where NF serves as an osmotic mass exchanger for water transport, and ED functions as an electric mass exchanger for salt transport. MTU analysis is employed for the NF-RO hybrid system, evaluating its overall efficiency, while MTU is individually applied to each stage of ED-NF. Applying MTU to existing hybrid systems, the total area and the effectiveness are obtained. The MTU values offer insights into system parameters and efficiency, and the effectiveness values are 50% for ED stage and 72% for NF stage. This comprehensive exploration contributes to the evolving understanding of hybrid desalination systems, leading to ways of enhanced water treatment solutions.

4.1. Introduction

Hybrid concept is an advanced approach applied widely in designing heat exchangers to optimize heat transfer in many applications. Hybrid heat exchangers aim to enhance overall efficiency by combining different mechanisms of heat exchangers, while the basic heat exchanger focuses on a single mode of heat transfer. Similarly, one of the modern desalination solutions to address many complex water desalination problems is using hybrid desalination systems, which attracted the attention of many researchers and engineers because it is a promising solution to many of the challenges associated with individual methods. These systems consist of integrating different desalination systems to optimize energy consumption and enhance efficiency.

There are different ways and configurations to design these hybrid systems depending on the design objective of the desalination unit. For example, Reverse Osmosis (RO) can be combined with a pretreatment stage such as nanofiltration (NF) electrodialysis (ED). Or NF can be combined with ED to reach the desired outcomes of the amount of treated water and its salinity. The MTU model is used for these integrated membrane processes to design, optimize, analyse, and evaluate the hybrid system as a complete mass exchanger unit by their recovery ratios, salt transport, and effectiveness.

4.2. Hybrid NF-RO effectiveness (ϵ -MTU model)

The integration of nanofiltration and reverse osmosis in a hybrid system is a modern solution for purifying concentrated water. NF and RO work sequentially to gradually treat salt water from impurities and dissolved materials. The types of these hybrid systems vary. There are two types, one of which is to be designed to treat filtered water continuously across all stages. This method is ideal for applications requiring high purity water required by some industries and applications. Alternatively, hybrid systems can be designed to treat first-stage reflux water and the integration

of NF and RO is designed to maximize water recovery from the concentrate stream, making it a suitable strategy for water conservation or reuse scenarios.

4.2.1. Integrated stages of NF and RO for high-purity water production

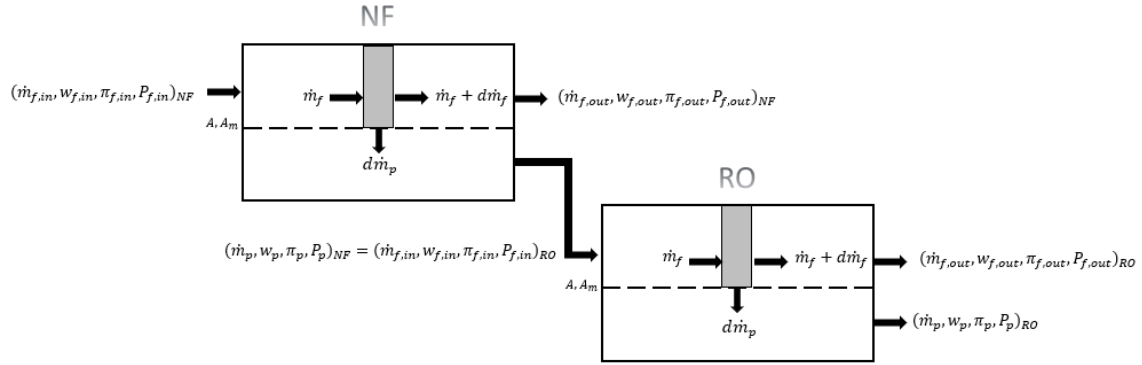


Fig. 4-1. Schematic drawing of NF-RO hybrid system for high purity production

NF is used as the first stage of the hybrid system that filters the water from ions and large particles before passing to RO stage. This initial purification step plays a crucial role in preventing fouling and scaling problems on the subsequent RO membrane. RO, as the second stage, is used to purify the water from smaller parts of salt by applying higher pressure. This system shows an effective process that produces water with very low salt concentration.

A schematic of the Nanofiltration-Reverse Osmosis (NF-RO) hybrid desalination system is represented in Fig. 4-1. Each stage of the NF-RO hybrid system contributes to the overall efficiency of reducing and purifying the water. The high salinity feed enters the system from the left side of the diagram that illustrates the inlet of NF stage. The water molecules and ions with small sizes pass through NF membranes, while large particles and organic molecules are prevented to transport to permeate side. The arrow connecting the NF and RO stages indicates the smooth transition of water from one phase to another within the hybrid system. On the right side of the diagram, we depict the RO stage, which follows the NF process. The partially treated water from

the NF stage is further purified by the RO membrane. This membrane operates at higher pressures, effectively removing smaller ions and contaminants, resulting in high-quality treated water.

Recall that the recovery ratio for a single unit of NF (RR_{NF}) or a single unit of RO (RR_{RO}) is the fraction of the produced flow rate to the feed flow rate.

$$RR_{NF} = \frac{\dot{m}_{p,NF}}{\dot{m}_{f,in,NF}} \quad (4.1)$$

$$RR_{RO} = \frac{\dot{m}_{p,RO}}{\dot{m}_{f,in,RO}} \quad (4.2)$$

The recovery ratio of the hybrid system can be defined as the permeate mass flow rate of the hybrid system that is collected from the outlet of RO stage over the hybrid feed mass flow rate of the hybrid system entering from the inlet of NF stage:

$$RR_{hrd} = \frac{\dot{m}_{p,hrd}}{\dot{m}_{f,in,hrd}} \quad (4.3)$$

$$RR_{hrd} = \frac{\dot{m}_{p,RO}}{\dot{m}_{f,in,NF}} \quad (4.4)$$

Also, the permeate flow rate of NF stage equals the flow rate of RO flow rate.

$$\dot{m}_{p,NF} = \dot{m}_{f,in,RO} \quad (4.5)$$

Applying Eq. (4.1), Eq. (4.2), and Eq. (4.4) to Eq. (4.3) leads to:

$$RR_{hrd} = \frac{\dot{m}_{p,RO}}{\dot{m}_{f,in,RO}} * \frac{\dot{m}_{p,NF}}{\dot{m}_{f,in,NF}} * \frac{\dot{m}_{f,in,RO}}{\dot{m}_{p,NF}} \quad (4.6)$$

Or,

$$RR_{hrd} = RR_{RO} * RR_{NF} \quad (4.7)$$

The effectiveness of the hybrid system can be defined as the ratio of the actual permeate flow rate produced by a certain size of the integrated mass exchanger to the maximum possible permeate flow rate for a given applied hydraulic pressure and an inlet feed osmotic pressure. This allows the definition also to be the actual recovery ratio of the system to the maximum recovery ratio. The effectiveness of the hybrid system is expressed as:

$$\varepsilon_{hrd} = \frac{RR_{hrd}}{RR_{hrd,max}} \quad (4.8)$$

Substitution of Eq. (4.7) into Eq. (4.8) yields:

$$\varepsilon_{hrd} = \frac{RR_{RO} * RR_{NF}}{RR_{hrd,max}} \quad (4.9)$$

Using the definition of effectiveness for NF and RO stages that was reached in NF mass exchanger analogy model (Eq. 2.23) and RO mass exchanger analogy model [12], the hybrid effectiveness can be expressed as:

$$\varepsilon_{hrd} = \frac{\varepsilon_{RO} RR_{RO,max} * \varepsilon_{NF} RR_{NF,max}}{RR_{hrd,max}} \quad (4.10)$$

The maximum recovery ratio of the hybrid system, $RR_{hrd,max}$, is reached when the maximum recovery of both stages, $RR_{NF,max}$ and $RR_{RO,max}$, are achieved:

$$RR_{hrd,max} = RR_{RO,max} * RR_{NF,max} \quad (4.11)$$

By applying Eq. (4.11) to Eq. (4.10), the effectiveness equation of the hybrid mass exchanger is expressed by the following equation:

$$\varepsilon_{hrd} = \varepsilon_{RO} * \varepsilon_{NF} \quad (4.12)$$

To have a certain expression for the maximum recovery ratio of the hybrid system, note that the maximum recovery ratio for RO stage is found as [12]:

$$RR_{RO,max} = 1 - SR_{f,RO} \quad (4.13)$$

Substitution Eq. (4.13), and the found expression of the maximum recovery ratio for NF system, Eq. (2.23), into Eq. (4.11) yields:

$$RR_{hrd,max} = (1 - SR_{f,RO})(1 - SR_{f,NF} + SR_{p,NF}) \quad (4.14)$$

4.2.2. Brine-Focused Integration of NF and RO hybrid system

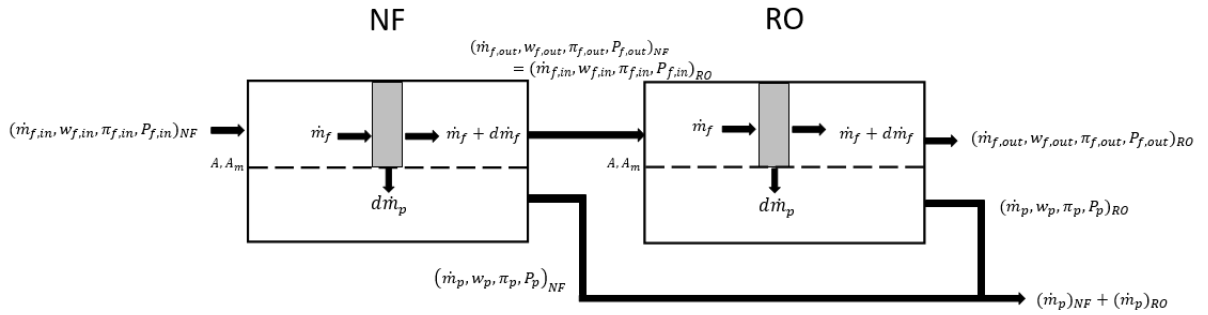


Fig. 4-2. Schematic drawing of NF-RO hybrid system for brine treatment

In this configuration (See Fig.4-2), feedwater enters the system from the Nanofiltration inlet as the initial stage of the hybrid. NF selectively removes impurities, allowing salt to pass through, resulting in a diluted permeate. The remaining brine of the NF stage is directed to the Reverse Osmosis stage. The RO stage further purifies the brine, separating water from the concentrated solutes, and producing additional permeate. The permeate from both NF and RO stages is collected. This approach maximizes water recovery while maintaining a high degree of purity in the collected permeate.

For this configuration, the recovery ratio of the hybrid system is defined as the total permeate mass flow rate that is collected from each stage of the hybrid system over the feed mass flow rate of the hybrid system entering from the inlet of NF stage:

$$RR_{hrd} = \frac{\dot{m}_{p,hrd}}{\dot{m}_{f,in,hrd}} \quad (4.15)$$

$$RR_{hrd} = \frac{\dot{m}_{p,RO} + \dot{m}_{p,NF}}{\dot{m}_{f,in,NF}} \quad (4.16)$$

Applying Eq. (4.1) and Eq. (4.2) to Eq. (4.16) leads to:

$$RR_{hrd} = RR_{NF} + RR_{RO} \times \frac{\dot{m}_{f,in,RO}}{\dot{m}_{f,in,NF}} \quad (4.17)$$

Since the feed of RO system is taken from the brine mass flow rate of NF:

$$RR_{hrd} = RR_{NF} + RR_{RO} \times \frac{\dot{m}_{f,out,NF}}{\dot{m}_{f,in,NF}} \quad (4.18)$$

Using the mass balance equation for NF stage:

$$\dot{m}_{f,NF,out} = \dot{m}_{f,NF,in} - \dot{m}_{p,NF} \quad (4.19)$$

Applying Eq. (4.19) to Eq. (4.18) yields:

$$RR_{hrd} = RR_{NF} + RR_{RO} * \frac{\dot{m}_{f,NF,in} - \dot{m}_{p,NF}}{\dot{m}_{f,NF,in}} \quad (4.20)$$

By applying the recovery ratio equation of NF, the hybrid recovery ratio of brine-based configuration is expressed as:

$$RR_{hrd} = RR_{NF} + RR_{RO} - RR_{RO}RR_{NF} \quad (4.21)$$

Using the definition of the effectiveness of the hybrid system as expressed in Eq. (4.8), the expression of the hybrid system is derived. Substitution of Eq. (4.21) into Eq. (4.8) yields:

$$\varepsilon_{hrd} = \frac{RR_{NF} + RR_{RO} - RR_{RO} \times RR_{NF}}{RR_{hrd,max}} \quad (4.22)$$

Using the definition of effectiveness for NF and RO stages that was reached in NF mass exchanger analogy model (Eq. 2.23) and RO mass exchanger analogy model [12], the hybrid effectiveness can be expressed as:

$$\varepsilon_{hrd} = \frac{\varepsilon_{NF}RR_{NF,max} + \varepsilon_{RO}RR_{RO,max} - \varepsilon_{RO}RR_{RO,max} \times \varepsilon_{NF}RR_{NF,max}}{RR_{hrd,max}} \quad (4.23)$$

The maximum recovery ratio of the hybrid system, $RR_{hrd,max}$, is reached when the maximum recovery of both stages, $RR_{NF,max}$ and $RR_{RO,max}$, are achieved:

$$RR_{hrd,max} = RR_{NF,max} + RR_{RO,max} - RR_{RO,max}RR_{NF,max} \quad (4.24)$$

By applying Eq. (4.24) to Eq. (4.23), the effectiveness equation of the hybrid mass exchanger is expressed by the following equation:

$$\varepsilon_{hrd} = \frac{\varepsilon_{NF}RR_{NF,max} + \varepsilon_{RO}RR_{RO,max} - \varepsilon_{RO} \varepsilon_{NF}RR_{NF,max}RR_{RO,max}}{RR_{NF,max} + RR_{RO,max} - RR_{RO,max}RR_{NF,max}} \quad (4.25)$$

Substitution Eq. (4.13), and the found expression of the maximum recovery ratio for NF system, Eq. (2.23), into Eq. (4.25) yields:

$$\varepsilon_{hrd} = \frac{\varepsilon_{NF}(1 - SR_{f,NF} + SR_{p,NF}) + \varepsilon_{RO}(1 - SR_{f,RO}) - \varepsilon_{RO} \varepsilon_{NF}(1 - SR_{f,NF} + SR_{p,NF})(1 - SR_{f,RO})}{(1 - SR_{f,NF} + SR_{p,NF}) + (1 - SR_{f,NF}) - (1 - SR_{f,RO})(1 - SR_{f,NF} + SR_{p,NF})} \quad (4.12)$$

4.3. Hybrid ED-NF effectiveness (ε -MTU model)

For Nanofiltration (NF) and Electrodialysis (ED) in a hybrid system, each mass exchanger has its own mass transfer characteristics. NF, acting as an osmotic mass exchanger, operates for transporting water through its semi-permeable membrane while rejecting salts. On the other hand,

ED functions as an electric mass exchanger, relying on the applied electric field to specifically transport ions of salt across its ion-selective membranes.

This difference in mass transfer mechanisms results in distinct Mass Transfer Units (MTU) for NF and ED within the hybrid system. The MTU for NF reflects its efficiency of producing water through its transporting while rejecting the salt. In contrast, the MTU for ED is related with its effectiveness by analyzing the transporting of ions.

4.3.1. Mass Transfer in the ED-NF Hybrid Configuration

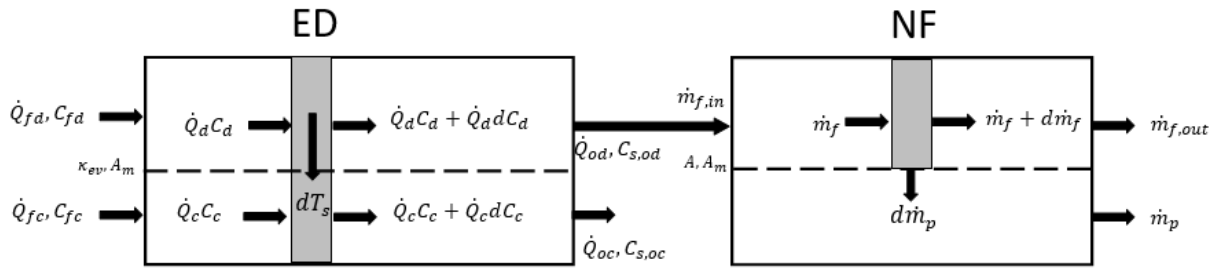


Fig. 4-3. Schematic drawing of ED-NF hybrid mass exchangers

The individual application of Mass Transfer Units (MTU) for each stage in a hybrid NF-ED or ED-NF system is one of the ways to design, evaluate, or modify the system. Given that NF primarily transports water and ED transports ions, the MTU for each process is inherently different. Applying MTU individually for each stage allows for a full understanding of the performance of NF and ED within the hybrid system. This customized method helps researchers and engineers improve the performance of each stage in the hybrid system. They can adjust how the system works and the features of the membranes for each part of the process. By looking at each stage separately using MTU, they get a detailed view of how well the system is purifying water and separating salt. This careful analysis helps in designing and improving the hybrid system for more efficient water treatment.

Strategic Optimization: Utilizing MTU Analysis for ED-NF Hybrid system:

Linh et al. have a study of desalination and removal of pesticides from surface water in Mekong Delta by coupling electrodialysis and nanofiltration [102]. A configuration that combines Electrodialysis (ED) and Nanofiltration (NF) processes is used, which is similar to Fig. 4-3 where the feed is first treated by ED before purifying it in NF stage. The objective of this study is to investigate this process for treatment.

A. ED stage

a. Nondimensionalizing ED system

In order to gain a comprehensive understanding of the Electrodialysis and Nanofiltration stages within the hybrid system, a preliminary step involves obtaining all non-dimensional values. For ED stage, the value of concentration ratio, CR, and resistance ratio, ER, are found as:

$$CR = \frac{C_{fd}}{C_{fc}} = \frac{2500}{9000} = 0.278$$

$$ER = \frac{C_{fd}}{\Delta/\Lambda r_{tot}} = \frac{2500}{0.5 / \left(\frac{10.5}{6000} \right) 0.00015} = 2.1875 * 10^{-3}$$

b. Desired permeate salinity

In the typical configuration, the first stage of a membrane-based desalination process often targets a specific rejection rate while achieving a designated salinity level in its permeate. This initial step sets the stage for the following one, i.e., NF. so that further adjustments and optimizations can be made to achieve the overall desalination goals. For this application, half of the salt is aimed to be removed from the permeate stream.

$$TR = \frac{C_s^\Delta}{C_{fd}} = \frac{0.5 * 5000}{5000} = 0.5$$

c. *MTU value*

Once these non-dimensional values are derived, they become the basis for calculating the Mass Transfer Units (MTU) specific each stage.

$$MTU = ER \times TR + \ln \left(\frac{1 + TR \times CR}{1 - TR} \right) = 0.82548$$

d. *Understanding and evaluating the system*

MTU value serves as a key indicator that allows us to design and understand the performance of the system, providing valuable insights into its functioning. For example, the area needed to reach this salinity before feeding it to NF stage can be determined as the following:

$$MTU = \frac{\zeta \Delta U_{tot} A}{\Delta z F \dot{Q}}$$

$$A = \frac{\Delta z F \dot{Q}}{\zeta \Delta U_{tot}} MTU = \frac{0.5 \times 1 \times 9.65 \times \frac{10^4}{60} * \frac{0.5}{1000 * 60}}{0.9 \times \frac{10.5}{60 \times 1000} * 15} 0.825 = 2.3415 m^2$$

Since each ED stack is combining 15 membranes of $64 cm^2$ each, the number of membranes, cell pairs, and stacks can be calculated as:

$$Number\ of\ Membranes: \frac{23.415 m^2}{64 cm^2} = 366\ membranes$$

$$Number\ of\ cell\ pairs = 183\ cell\ pairs$$

$$Number\ of\ stacks = 25\ stacks$$

e. *ED effectiveness*

The effectiveness of the first stage of the hybrid system can be evaluated as:

$$MTU = \varepsilon \times ER + \ln \frac{1 + CR \times \varepsilon}{1 - \varepsilon}$$

$$\varepsilon_{ED} = 0.5$$

B. NF stage

a. *Feed salinity for NF stage*

Using concentration factor of permeate side for ED stage:

$$CF_d = 1 - TR = 0.5$$

So the outlet salinity is:

$$C_{od} = C_{fd} \times CF_d = 2500 \text{ ppm}$$

As a result, the feed salinity of NF stage is:

$$w_{f,in} = C_{od} = 2500 \text{ ppm}$$

b. *Nondimensionalizing ED system*

To make the system non dimensional, the following calculations are conducted:

For recovery ratio of the stage:

$$RR_{NF} = \frac{0.237}{0.474} = 0.5$$

For osmotic pressures of the system:

$$SR_f = \frac{C w_{f,in}}{\Delta P} = \frac{73.45 \times 2.5}{500} = 0.367$$

$$SR_p = \frac{C w_p}{\Delta P} = \frac{73.45 \times 0.374}{500} = 0.055$$

f. *MTU value*

$$MTU = RR + (SR_f - SR_p) \ln \left(\frac{SR_f - SR_p - 1}{RR + SR_f - SR_p - 1} \right) = 0.905$$

g. Understanding and evaluating the system

Using the MTU model equations, the required membrane area of the stage can be calculated as:

$$MTU = \frac{AA_m \Delta P}{\dot{m}_{f,in}}$$

$$A = \frac{\dot{m}_{f,in,NF}}{A \Delta P} MTU$$

$$A = \frac{\frac{7.9 * 60}{1000}}{9 \times 10^{-5} \times 500} 0.905 = 9.533 m^2$$

$$Number\ of\ Membranes: \frac{9.533 m^2}{140 cm^2} = 681\ membranes$$

h. Salt passage and rejection

Salt passage and rejection is calculated as the following:

$$SP = \frac{0.055}{0.367} = 0.15$$

$$S_{rej} = 1 - SP = 0.85$$

i. Brine salinity

MTU model is also able to evaluate the brine salinity as:

$$w_{brine,NF} = C_{fd}(1 - TR) \frac{1 - RR_{NF} \left(\frac{SR_p}{SR_f} \right)_{NF}}{1 - RR_{NF}}$$

$$w_{brine,NF} = 2.5 \frac{1 - 0.5 \left(\frac{0.055}{0.367} \right)_{NF}}{1 - 0.5} = 4.625\ g/kg$$

- j. The effectiveness of the first stage of the hybrid system can be evaluated as:

$$MTU_{NF} = \varepsilon(1 - SR_f + SR_p) - (SR_f - SR_p) \ln(1 - \varepsilon)$$

$$\varepsilon_{NF} = 0.727$$

4.4. Conclusion

The extensive use of hybrid desalination systems is highlighted, reflecting how efficient they are in water treatment. Through the application of Mass Transfer Units (MTU) analysis, the study investigated the performance of combined processes such as NF and RO in different configurations depending on the need. An overall effectiveness has been developed for the system since both osmotic mass exchangers have the same concept of mass transfer ratio. Additionally, the examination of ED and NF showcased unique mass transfer dynamics. The MTU analysis revealed overall system efficiency, with specific effectiveness values of 50% for the ED stage and 72.7% for the NF stage. The reason for the individual study of ED and NF effectiveness lies in their inherent differences: ED is evaluated by chemical effectiveness that is based on chemical transport, while NF is evaluated by hydraulic effectiveness that is related to water transport and recovery ratio. It is recommended to develop an overall expression for effectiveness, considering each stage to be combined, and aiming for an overall understanding of the system's performance.

Appendix A

MTU for Nanofiltration mass exchanger

The MTU parameter is an analogy of the NTU method in heat exchangers, and it is used for analyzing the design and performance of mass exchangers. The NF mass exchanger can be designed and optimized using the MTU approach. MTU is a helpful tool for estimating mass transfer effectiveness and creating more effective mass transfer systems. The MTU parameter can be derived in a manner similar to the NTU derivation method.

The NTU equation was derived using the energy balance equation for each fluid stream in the heat exchanger. For a NF mass exchanger, the permeate flow through a differential membrane area is expressed as in Eq. (1). By applying a mass balance on the feed side of the mass exchanger using Fig. 2, we get:

$$\begin{aligned}\dot{m}_{in} - \dot{m}_{out} &= 0 \\ \dot{m}_f - (\dot{m}_f + d\dot{m}_f) - d\dot{m}_p &= 0 \\ d\dot{m}_p &= -d\dot{m}_f\end{aligned}\tag{A.1}$$

Substituting $d\dot{m}_p$ from Eq.(1) gives:

$$d\dot{m}_f = -A * (\Delta P - \Delta\pi) dA_m\tag{A.2}$$

For the permeate side, the permeate flow rate is given as:

$$d\dot{m}_p = A * (\Delta P - \Delta\pi) dA_m\tag{A.3}$$

The difference between Eq. (A.2) and Eq. (A.3) leads to

$$d(\dot{m}_f - \dot{m}_p) = [-2]A * (\Delta P - \Delta\pi) dA_m\tag{A.4}$$

Note that, at the inlet of the stream channel, the net driving force (the pressure difference between the Hydraulic pressure and osmotic pressure is at a maximum point (i.e. $\Delta P - \Delta\pi = \Delta P$) and the permeate flow rate is still zero.

$$d(\dot{m}_{f,in}) = A\Delta P dA_m [-2] \quad (\text{A.5})$$

To make Eq. (A.5) non-dimensional, both sides are divided by $\dot{m}_{f,in}$,

$$\frac{d(\dot{m}_{f,in})}{\dot{m}_{f,in}} = \frac{A\Delta P}{\dot{m}_{f,in}} dA_m [-2] \quad (\text{A.6})$$

Integrating both sides, we get

$$\ln(\dot{m}_{f,in}) = \frac{AA_m\Delta P}{\dot{m}_{f,in}} [-2] \quad (\text{A.7})$$

It can be seen that the previous steps as well as the result are completely similar to the method used to reach the NTU parameter [103]. In line with this method, it can be seen that

$$MTU = \frac{AA_m\Delta P}{\dot{m}_{f,in}} \quad (\text{A.8})$$

It should be noted that the total membrane area is analogous to the total surface area of a heat exchanger, and it determines the available surface for mass transfer. Also, the water permeability coefficient is analogous to the overall heat transfer coefficient, which shows how efficient is the transfer of the mass across the membrane surface.

Appendix B

MTU for Electrodialysis mass exchanger

The MTU parameter is an analogy of the NTU method in heat exchangers, and it is used for analyzing the performance of mass exchangers. ED mass exchangers can be designed and optimized using the MTU approach. MTU is a helpful tool for estimating mass transfer effectiveness and creating more effective mass transfer systems. The MTU parameter can be derived using the NTU derivation method.

The NTU equation was derived using the energy balance equation for each fluid stream in the heat exchanger. For ED mass exchanger, the salt transport equation is expressed in Eq. (3.3). By applying a mass balance on the feed side of the mass exchanger using Fig. 3-3, which considers low salinity water treatment that neglects water transport through the membranes:

For diluted side:

$$\dot{m}_{in} - \dot{m}_{out} = 0$$

$$\dot{Q}_p C_d - \dot{Q}_p (C_d + dC_d) - dT_s = 0$$

$$dT_s = -\dot{Q}_p dC_d \quad (B.1)$$

Substituting Eq. (3.3) gives:

$$\left(\frac{\zeta}{2\Delta z F}\right) \kappa_{av} U_{tot} dA = -\dot{Q}_p dC_d$$

$$dC_d = \frac{-\left(\frac{\zeta}{2\Delta z F}\right) \kappa_{av} U_{tot} dA}{\dot{Q}_p} \quad (B.2)$$

For the concentrate side:

$$\dot{m}_{in} - \dot{m}_{out} = 0$$

$$\dot{Q}_c C_c - \dot{Q}_c (C_c + dC_c) + dT_s = 0$$

$$dT_s = \dot{Q}_c dC_c \quad (B.3)$$

By substituting Eq. (3.3) into Eq. (B.2), we get

$$\left(\frac{\zeta}{2\Delta z F} \right) \kappa_{av} U_{tot} dA = \dot{Q}_c dC_c$$

$$dC_c = \frac{\left(\frac{\zeta}{2\Delta z F} \right) \kappa_{av} U_{tot} dA}{\dot{Q}_c} \quad (B.4)$$

Taking the difference between Eq. (B.3) and Eq. (B.4), we get

$$d(C_c - C_d) = \left(\frac{\zeta}{2\Delta z F} \right) \kappa_{av} U_{tot} dA \left[\frac{1}{\dot{Q}_p} + \frac{1}{\dot{Q}_c} \right] \quad (B.5)$$

The electrical conductivity (κ_{av}) is substituted using Eq. (3.5), which gives:

$$d(C_c - C_d) = \left(\frac{\zeta}{2\Delta z F} \right) \frac{2\Delta}{\left[\frac{\Delta}{\Lambda C_c} + \frac{\Delta}{\Lambda C_d} + r_{tot} \right]} U_{tot} dA \left[\frac{1}{\dot{Q}_p} + \frac{1}{\dot{Q}_c} \right] \quad (B.6)$$

Rearranging the equation yields:

$$\left[\frac{1}{C_c} + \frac{1}{C_d} \right] d(C_c - C_d) + \frac{\Lambda r_{tot}}{\Delta} d(C_c - C_d) = \left(\frac{\zeta \Lambda U_{tot}}{\Delta z F} \right) dA \left[\frac{1}{\dot{Q}_p} + \frac{1}{\dot{Q}_c} \right] \quad (B.7)$$

The concentration of both streams at any point can be substituted using the salt balance (Eq. (3.4)):

$$\begin{aligned} & \left[\frac{1}{C_{fc} + C_s^\Delta} + \frac{1}{C_{fd} - C_s^\Delta} \right] d((C_{fc} + C_s^\Delta) - (C_{fd} - C_s^\Delta)) + \frac{\Lambda r_{tot}}{\Delta} d((C_{fc} + C_s^\Delta) - (C_{fd} - C_s^\Delta)) \\ &= \left(\frac{\zeta \Lambda U_{tot}}{\Delta z F} \right) dA \left[\frac{1}{\dot{Q}_p} + \frac{1}{\dot{Q}_c} \right] \end{aligned} \quad (B.8)$$

Note that the water transport is neglected for the case of brackish water ED treatment (i.e. $\dot{Q}_p = \dot{Q}_c = \dot{Q}_{fp} = \dot{Q}_{fc} = \dot{Q}$), so the RHS of the above equation becomes:

$$\left(\frac{\zeta \Lambda U_{tot}}{\Delta z F} \right) dA \left[\frac{2}{\dot{Q}} \right] \quad (B.9)$$

By rearranging and taking the derivative of both sides, the result of the RHS leads to:

$$\left(\frac{\zeta \Lambda U_{tot} A}{\Delta z F \dot{Q}} \right) [2] \quad (B.10)$$

It can be seen that the previous steps and the result in Eq. (B.10) are completely similar to the method used to reach the NTU parameter [104]. This means that

$$MTU = \frac{\zeta \Lambda U_{tot} A}{\Delta z F \dot{Q}} \quad (B.11)$$

Now, by applying a mass balance on the feed side of the mass exchanger using Fig. 3-7, which considers water transport for high salinity water treatment, the MTU can be found by the following procedure. Consider the mass balance for diluted side as:

$$\begin{aligned} \dot{m}_{in} - \dot{m}_{out} &= 0 \\ \dot{Q}_p C_d - (\dot{Q}_p C_d + d\dot{Q}_p C_d) - dT_s &= 0 \\ dT_s &= \dot{Q}_f dC_s^\Delta = -d\dot{Q}_p C_d \end{aligned} \quad (B.12)$$

Substituting Eq. (3.3) into Eq. (B.12) gives:

$$\left(\frac{\zeta}{2\Delta z F}\right) \kappa_{av} U_{tot} dA = -\dot{Q}_p dC_d$$

$$d(\dot{Q}_p C_d) = -\left(\frac{\zeta}{2\Delta z F}\right) \kappa_{av} U_{tot} dA \quad (B.13)$$

The mass balance for the concentrate side is given as:

$$\dot{m}_{in} - \dot{m}_{out} = 0$$

$$\dot{Q}_c C_c - (\dot{Q}_c C_c + d\dot{Q}_c C_c) + dT_s = 0$$

$$dT_s = d\dot{Q}_c C_c \quad (B.14)$$

Substituting Eq. (3.3) into Eq. (B.14) gives:

$$\left(\frac{\zeta}{2\Delta z F}\right) \kappa_{av} U_{tot} dA = d\dot{Q}_c C_c$$

$$d\dot{Q}_c C_c = \left(\frac{\zeta}{2\Delta z F}\right) \kappa_{av} U_{tot} dA \quad (B.15)$$

By taking the difference between Eq. (B.13) and Eq. (B.15):

$$d(\dot{Q}_c C_c - \dot{Q}_d C_d) = [2] \left(\frac{\zeta}{2\Delta z F}\right) \kappa_{av} U_{tot} dA \quad (B.16)$$

The electrical conductivity (κ_{av}) is substituted using Eq. (3.23) and rearranging:

$$\left[\frac{1}{C_c} + \frac{1}{C_d}\right] d(\dot{Q}_c C_c - \dot{Q}_d C_d) + \frac{\Lambda r_{tot}}{(\Delta - 2\delta)} d(\dot{Q}_c C_c - \dot{Q}_d C_d) = [2] \left(\frac{\zeta \Lambda U_{tot}}{(\Delta - 2\delta) z F \beta}\right) dA \quad (B.17)$$

The concentration of both streams at any point can be substituted using the salt balance i.e. Eq.

(3.21):

$$\left[\frac{\dot{Q}_f(2-R)}{T_s + C_{fc}\dot{Q}_{fc}} + \frac{R\dot{Q}_f}{C_{fd}\dot{Q}_{fd} - T_s}\right] d((\dot{Q}_c C_c - \dot{Q}_d C_d) + \frac{\Lambda r_{tot}}{(\Delta - 2\delta)} d(\dot{Q}_c C_c - \dot{Q}_d C_d)$$

$$= [2] \left(\frac{\zeta \Lambda U_{\text{tot}}}{(\Delta - 2\delta) z F} \right) dA \quad (B.18)$$

By dividing $\dot{Q}_f$ and taking the derivative for both sides, the RHS becomes:

$$[2] \left(\frac{\zeta \Lambda U_{\text{tot}} A}{\dot{Q}_f (\Delta - 2\delta) z F} \right) \quad (B.19)$$

It can be seen that the previous steps and the result in Eq. (B.19) are completely similar to the method used to reach the NTU parameter [104]. This means that

$$MTU = \frac{\zeta \Lambda U_{\text{tot}} A}{\dot{Q}_f (\Delta - 2\delta) z F} \quad (B.20)$$

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