UNIVERSITY OF PARDUBICE

FACULTY OF CHEMICAL TECHNOLOGY

Institute of Environmental and Chemical Engineering

Vojtěch Štěpánek

Numerical Analysis of Dialysis with Chemical Reaction

Theses of the Doctoral Dissertation

Pardubice 2020

Study program: **Chemical and Process Engineering**

Study field: **Chemical Engineering**

Author: **Vojtěch Štěpánek**

Supervisor: **doc. Ing. Zdeněk Palatý, CSc.**

Year of the defence: 2020

References

ŠTĚPÁNEK, Vojtěch. *Numerical Analysis of Dialysis with Chemical Reaction.* Pardubice, 2020. 147 pages. Dissertation thesis (Ph.D.). University of Pardubice, Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering. Supervisor Doc. Ing. Zdeněk Palatý, CSc.

Abstract

The dissertation deals with the mathematical modeling and numerical analysis of dialysis accompanied by a second-order chemical reaction that takes place in the membrane or in the stripping solution. The study of dialysis accompanied by a chemical reaction in the membrane makes use of the analogy with the process of absorption with chemical reaction. The effect of the chemical reaction on the transport rate of a solute in the membrane is quantified in terms of the enhancement factor. The work also includes the comparison of approximate solutions for the enhancement factor available in the literature for the case of absorption accompanied by a fast irreversible second-order reaction with the results of the exact numerical solution. A continuous counter-current arrangement was chosen for the study of dialysis accompanied by a chemical reaction in the stripping solution. The effect of a chemical reaction on the extraction ratio of the transported solute in a dialyzer was studied with the use of the rigorous mathematical model of a continuous counter-current dialyzer and the simplified model based on the utilization of the concept of the enhancement factor.

Abstrakt

Disertační práce se zabývá matematickým modelováním a numerickou analýzou dialýzy, která je doprovázena chemickou reakcí druhého řádu probíhající v membráně nebo stripovacím roztoku. Studium dialýzy doprovázené chemickou reakcí v membráně je založeno na využití analogie s procesem absorpce s chemickou reakcí. Vliv chemické reakce na rychlost transportu složky membránou je kvantifikován pomocí reakčního faktoru. Součástí práce je také porovnání přesnosti přibližných řešení pro reakční faktor publikovaných v literatuře pro případ absorpce doprovázené rychlou nevratnou reakcí druhého řádu s výsledky přesného numerického řešení. Pro studium dialýzy doprovázené chemickou reakcí ve stripovacím roztoku bylo zvoleno kontinuální protiproudé uspořádání. Vliv chemické reakce na účinek dialyzéru byl studován s využitím exaktního matematického modelu kontinuálního protiproudého dialyzéru a zjednodušeného modelu založeného na využití konceptu reakčního faktoru.

Keywords

Dialysis, chemical reaction, reactive absorption, enhancement factor, continuous dialyzer, numerical analysis.

Klíčová slova

Dialýza, chemická reakce, reaktivní absorpce, reakční faktor, kontinuální dialyzér, numerická analýza.

Table of contents

Introduction

Dialysis belongs to the group of membrane separation processes, which are based on the utilization of semipermeable membranes. In dialysis, the transport of solutes through the membrane takes place as a consequence of a concentration difference between solutions on both sides of the membrane. The main advantage of dialysis are low energy requirements for separation, which is related to the fact that the separation is not accompanied by a phase change and the process is usually carried out at common temperatures and pressures. The main disadvantage of dialysis is a generally low intensity of solute transport through the membrane, which is related to the fact that the mass transfer is controlled by diffusion of components inside the membrane and the sole driving force, i.e., the concentration difference, is often relatively low.

The mass transfer rate can be increased by the addition of a reactive component into the stripping solution, which chemically reacts with the component transported through the membrane. The chemical reaction can take place in the membrane or in the stripping solution. Practical applications of this concept include dialysis of phenols and anilines into the stripping solutions containing sodium hydroxide or inorganic acids, respectively, using nonporous hydrophobic membranes [1–5] and neutralization dialysis of carboxylic acids [6, 7], phenol [6, 8] and glycine [9] into the stripping solutions containing sodium hydroxide using anion-exchange membranes.

Mass transfer processes accompanied by chemical reactions have received a lot of interest from researchers. Up to now, most attention has been paid to the mass transfer in gas–liquid systems accompanied by a reaction in a liquid film, namely reactive absorption. The effect of a chemical reaction on the mass transfer rate has been traditionally expressed in terms of the enhancement factor E, which is defined as the ratio of the mass transfer rate in the presence of a chemical reaction to that in the absence of a chemical reaction under otherwise identical conditions. Exact analytical solution of these models is available only for a limited number of cases, e.g., for first-order or instantaneous reactions. However, a number of approximate analytical solutions are available in the literature for the enhancement factor for absorption accompanied by a chemical reaction.

The first part of the doctoral dissertation deals with absorption accompanied by an irreversible second-order reaction. Here, a thorough review of the existing approximate analytical solutions for the enhancement factor is presented. The second part deals with dialysis accompanied by an irreversible second-order reaction that takes place in the membrane. A simple scheme, in which component A is transported through a nonporous membrane by diffusion and reacts with component B diffusing in the opposite direction, is considered. Approximate analytical solutions for the enhancement factor are developed based on the analysis of limiting cases and the analogy between the mass transfer in the membrane in case of dialysis and that in the liquid film in case of absorption, both accompanied by an irreversible second-order reaction. The third part deals with continuous counter-current dialysis accompanied by a second-order reaction (both irreversible and reversible) that takes place in the stripping solution. The enhancement in the extraction ratio of the transported component due to a chemical reaction in the stripping solution is analyzed here.

1. Current state of research

1.1 Absorption accompanied by irreversible second-order reaction

Many industrial processes involve reactive absorption, in which mass transfer of the absorbed component through the gas–liquid interface is followed by a chemical reaction in the liquid phase. The chemical reaction can significantly enhance the rate of absorption and increase the capacity of absorbent compared to physical absorption. Three mass transfer theories have been traditionally employed to describe mass transfer in gas–liquid systems accompanied by a chemical reaction, namely the film, penetration and surface renewal theories [10, 11]. Although the film theory represents a rather simplified model, its applicability for description of mass transfer in gas–liquid system has been proven many times and due to its simplicity, this theory is still preferred by many researchers [12, 13].

For mass transfer in gas–liquid systems accompanied by an irreversible second-order reaction $A + v_B B \rightarrow v_P P$, the steady-state differential mass balance of the reacting components in the liquid film at the gas–liquid interface based on the film theory can be written as follows:

$$D_A \frac{d^2 c_A}{dx^2} - k_2 c_A c_B = 0 \tag{1}$$

$$D_B \frac{d^2 c_B}{dx^2} - v_B k_2 c_A c_B = 0 \tag{2}$$

where D_i is the diffusion coefficient and c_i is the molar concentration of the respective component in the liquid film (i = A, B), x is the spatial coordinate, k_2 is the second-order reaction rate constant and v_B is the stoichiometric coefficient. The boundary conditions for Eqs (1) and (2) are

$$x = 0: \qquad c_A = c_{A,0} \qquad \frac{dc_B}{dx} = 0 \tag{3a,b}$$

$$x = \delta_L: \qquad c_A = 0 \qquad c_B = c_{B,\delta} \tag{4a,b}$$

where $c_{A,0}$ is the concentration of component A at the gas–liquid interface, $c_{B,\delta}$ is the bulk concentration of component B and δ_L is the thickness of the liquid film. The boundary condition (3b) assumes that component B is present solely within the liquid phase and cannot pass through the gas–liquid interface. The boundary condition (4a) assumes that component A is completely consumed within the liquid film (fast reaction regime). Introducing the dimensionless spatial coordinate $X = x/\delta_L$ and relative concentrations of both reacting components in the liquid film $[A] = c_A/c_{A,0}$ and $[B] = c_B/c_{B,\delta}$, Eqs (1) and (2) can be transformed into the dimensionless forms

$$\frac{d^2 [A]}{dX^2} - Ha^2 [A][B] = 0 \tag{5}$$

$$\frac{d^2 [B]}{dX^2} - \frac{Ha^2}{E_2^\infty - 1} [A][B] = 0 \tag{6}$$

In Eqs (5) and (6), Ha denotes the dimensionless Hatta number and E_2^∞ denotes the enhancement factor corresponding to an instantaneous irreversible second-order reaction $A + \nu_B B \rightarrow \nu_P P$ that takes place in the liquid film

$$Ha = \delta_L \sqrt{\frac{k_2 c_{B,\delta}}{D_A}} \qquad E_2^\infty = 1 + \frac{D_B c_{B,\delta}}{\nu_B D_A c_{A,0}} \qquad (7a,b)$$

The transformed boundary conditions become

$$X = 0: \qquad [A] = 1 \qquad \frac{d[B]}{dX} = 0 \qquad (8a,b)$$

$$X = 1: \qquad [A] = 0 \qquad [B] = 1 \qquad (9a,b)$$

Exact analytical solution of Eqs (5) and (6) with boundary conditions (8a,b) and (9a,b) in terms of the enhancement factor is only available for several limiting cases:

- Very slow reaction – enhancement factor $E_2 \doteq 1$

- Instantaneous reaction – enhancement factor E_2^∞ given by Eq. (7b)

- Pseudo-first-order reaction – enhancement factor for the film theory ($E_{1,film}$), surface renewal theory ($E_{1,s-r}$) and penetration theory ($E_{1,pen}$) given as follows [10]:

$$E_{1,film} = \frac{Ha}{\tanh Ha} \qquad\qquad E_{1,s-r} = \sqrt{1 + Ha^2} \qquad (10a,b)$$

$$E_{1,pen} = \left(Ha + \frac{\pi}{8Ha}\right) \text{erf}\left(\frac{2Ha}{\sqrt{\pi}}\right) + \frac{1}{2}\exp\left(-\frac{4Ha^2}{\pi}\right) \qquad (11)$$

As no analytical solution exists for a general case of an irreversible second-order reaction, an effort has been made in the past to derive approximate expressions for the enhancement factor in order to avoid the necessity of numerical solution of differential equations (5) and (6) with boundary conditions (8a,b) and (9a,b). These approximate analytical solutions are presented in Tab. 1.

The literature review has revealed that despite the big effort devoted to the development of the approximate solutions, only limited attention had been paid to evaluation of the accuracy of these approximate solutions. De Santiago and Farina [18] presented a numerical solution of Eqs (5) and (6) with boundary conditions (8a,b) and (9a,b) and provided the values of the enhancement factor for 54 combinations of parameters Ha and E_2^∞, out of which 25 combinations fall into the regions governed by limiting cases, i.e., instantaneous and pseudo-first-order reactions for $Ha > 10 \times E_2^\infty$ and $Ha < 0.1 \times E_2^\infty$, respectively. Wellek et al. [22] used the values of the enhancement factor previously published by de Santiago and Farina for evaluation of accuracy of their own approximate solution and eight approximate solutions available in the literature at that time (see Tab. 1). Such an evaluation was not performed for the approximate solutions of Karlsson and Bjerle [23] and Last and Stichlmair [24] as these were compared with the results of the approximate solution of van Krevelen and Hoftijzer [14] only.

Tab. 1: Overview of approximate analytical solutions for enhancement factor for irreversible second-order reaction

Author	Expression	Form Model [a] Limitation
van Krevelen and Hoftijzer [14] (1948)	$E_2 = \dfrac{\gamma}{\tanh \gamma}\,, \qquad$ where $\gamma = Ha \sqrt{\dfrac{E_2^\infty - E_2}{E_2^\infty - 1}}$	Implicit Film None
Hikita and Asai [15] (1964)	$E_2 = \left(\gamma + \dfrac{\pi}{8\gamma}\right)\mathrm{erf}\left(\dfrac{2\gamma}{\sqrt{\pi}}\right) + \dfrac{1}{2}\exp\left(-\dfrac{4\gamma^2}{\pi}\right),$ where $\gamma = Ha \sqrt{\dfrac{E_2^\infty - E_2}{E_2^\infty - 1}}$	Implicit Penetration None
Porter [16] (1966)	$E_2 = 1 + (E_2^\infty - 1)\left[1 - \exp\left(-\dfrac{Ha - 1}{E_2^\infty - 1}\right)\right]$	Explicit N/A $Ha > 2$
Yeramian et al. [17] (1970)	$E_2 = -\dfrac{E_1^2}{2(E_2^\infty - 1)} + \sqrt{\dfrac{E_1^4}{4(E_2^\infty - 1)^2} + \dfrac{E_2^\infty E_1^2}{E_2^\infty - 1}}$	Explicit All [b] None
de Santiago and Farina [18] (1970)	$E_2 = -\dfrac{Ha^2}{2(E_2^\infty - 1)} + \sqrt{\dfrac{Ha^4}{4(E_2^\infty - 1)^2} + \dfrac{Ha^2}{E_2^\infty - 1} + Ha^2}$	Explicit Film $E_2 > 3$
Kishinevskii et al. [19] (1971)	$E_2 = 1 + \dfrac{Ha}{\alpha}\left[1 - \exp\left(-0.65\, Ha\sqrt{\alpha}\right)\right],$ where $\alpha = \dfrac{Ha}{E_2^\infty - 1} + \exp\left(\dfrac{0.68}{Ha} - \dfrac{0.45\, Ha}{E_2^\infty - 1}\right)$	Explicit N/A None
DeCoursey [20] (1974)	$E_2 = -\dfrac{Ha^2}{2(E_2^\infty - 1)} + \sqrt{\dfrac{Ha^4}{4(E_2^\infty - 1)^2} + \dfrac{E_2^\infty Ha^2}{E_2^\infty - 1} + 1}$	Explicit Surf. renewal None
Baldi and Sicardi [21] (1975)	$E_2 = 1 + (E_2^\infty - 1)\left[1 - \exp\left(-\dfrac{\sqrt{1 + Ha^2} - 1}{E_2^\infty - 1}\right)\right]$	Explicit N/A None
Wellek et al. [22] (1978)	$\left(\dfrac{1}{E_2 - 1}\right)^{1.35} = \left(\dfrac{1}{E_2^\infty - 1}\right)^{1.35} + \left(\dfrac{1}{E_1 - 1}\right)^{1.35}$	Explicit Film None
Karlsson and Bjerle [23] (1980)	$E_2 = \dfrac{\left[Ha^{-3/2} + (E_2^\infty)^{-3/2}\right]^{-2/3}}{\tanh\left[Ha^{-3/2} + (E_2^\infty)^{-3/2}\right]^{-2/3}}$	Explicit Film $E_2^\infty > 2$
Last and Stichlmair [24] (2002)	$E_2 = \left[\dfrac{1 - 1/E_2^\infty}{Ha^{3/2}} + \dfrac{1}{(E_2^\infty)^{3/2}}\right]^{-2/3}$	Explicit N/A $Ha > 2$

[a] As defined by original authors
[b] Based on expression for E_1 used
N/A Not specifically mentioned or ambiguous

1.2 Dialysis accompanied by irreversible second-order reaction in membrane

Mass transfer through dialysis membranes is usually described by the solution–diffusion model [25, 26]. According to this model, transported components dissolve in the membrane material and diffuse down a concentration gradient. As the mass transfer is controlled by diffusion of components inside the membrane, the separation process is generally very slow. The mass transfer rate can be increased by the addition of a reactive component into the stripping solution, which chemically reacts with the component transported through the membrane. Here, transport of component A is assumed through a nonporous membrane from the feed solution (compartment I) to the stripping solution (compartment II), which reacts with component B diffusing in the opposite direction according to an irreversible second-order reaction $A + \nu_B B \rightarrow \nu_P P$ that takes place in the membrane. The steady-state differential mass balance of the reacting components in the membrane can be written as follows:

$$D_{AM} \frac{d^2 c_{AM}}{dx^2} - k_2 c_{AM} c_{BM} = 0 \tag{12}$$

$$D_{BM} \frac{d^2 c_{BM}}{dx^2} - \nu_B k_2 c_{AM} c_{BM} = 0 \tag{13}$$

where D_{iM} is the diffusion coefficient and c_{iM} is the molar concentration of the respective component in the membrane (i = A, B), x is the spatial coordinate, k_2 is the second-order reaction rate constant and ν_B is the stoichiometric coefficient. Eqs (12) and (13) are formally identical to Eqs (1) and (2) that describe mass transfer in gas–liquid systems accompanied by an irreversible second-order reaction in the liquid film, though the boundary conditions are different. General boundary conditions for Eqs (12) and (13) can be written as

$$x = 0: \qquad c_{AM} = \Psi_A^I c_A^I \qquad c_{BM} = \Psi_B^I c_B^I \tag{14a,b}$$

$$x = \delta_M: \qquad c_{AM} = \Psi_A^{II} c_A^{II} \qquad c_{BM} = \Psi_B^{II} c_B^{II} \tag{15a,b}$$

where Ψ_i^j (i = A, B; j = I, II) is the partition coefficient, c_A^I and c_B^{II} are the bulk concentrations and δ_M is the membrane thickness. In case of a fast reaction, the concentration of the transported component in the stripping solution and that of the reactive component in the feed may become negligible and the boundary conditions for Eqs (12) and (13) become

$$x = 0: \qquad c_{AM} = \Psi_A^I c_A^I \qquad c_{BM} = 0 \tag{16a,b}$$

$$x = \delta_M: \qquad c_{AM} = 0 \qquad c_{BM} = \Psi_B^{II} c_B^{II} \tag{17a,b}$$

Nagy [26] presented a quasi-analytical solution of Eqs (12) and (13) with general boundary conditions (14a,b) and (15a,b), which consists in dividing the membrane into sublayers and assuming the concentration of the other reactant to be constant in each sublayer. Eqs (12) and (13) can then be solved analytically. However, this approach does not provide any significant advantage over conventional numerical solution methods for the boundary value problems.

Introducing the dimensionless spatial coordinate $X = x/\delta_M$ and relative concentrations of both reacting components in the membrane $[A_M] = c_{AM}/\Psi_A^I c_A^I$ and $[B_M] = c_{BM}/\Psi_B^{II} c_B^{II}$, Eqs (12) and (13) can be transformed into the dimensionless forms

$$\frac{d^2[A_M]}{dX^2} - Ha_M^2 [A_M][B_M] = 0 \tag{18}$$

$$\frac{d^2[B_M]}{dX^2} - \frac{Ha_M^2}{E_{2M}^\infty - 1}[A_M][B_M] = 0 \tag{19}$$

In Eqs (18) and (19), Ha_M denotes the dimensionless Hatta number and E_{2M}^∞ denotes the enhancement factor corresponding to an instantaneous irreversible second-order reaction $A + \nu_B B \rightarrow \nu_P P$ that takes place in the membrane

$$Ha_M = \delta_M \sqrt{\frac{k_2 \Psi_B^{II} c_B^{II}}{D_{AM}}} \qquad E_{2M}^\infty = 1 + \frac{D_{BM} \Psi_B^{II} c_B^{II}}{\nu_B D_{AM} \Psi_A^I c_A^I} \tag{20a,b}$$

The transformed boundary conditions in case of a fast reaction become

$$X = 0: \qquad [A_M] = 1 \qquad [B_M] = 0 \tag{21a,b}$$

$$X = 1: \qquad [A_M] = 0 \qquad [B_M] = 1 \tag{22a,b}$$

Exact analytical solution of Eqs (18) and (19) with boundary conditions (21a,b) and (22a,b) in terms of the enhancement factor is only available for the limiting cases of a very slow reaction ($E_{2M} \doteq 1$) and an instantaneous reaction (E_{2M}^∞ given by Eq. (20b)). Furthermore, an additional limiting case can be considered that is characterized by linear concentration profile of reactive component B in the membrane ($[B_M] = X$). The corresponding differential mass balance of component A in the dimensionless form can be written as

$$\frac{d^2[A_M]}{dX^2} - Ha_M^2 [A_M] X = 0 \tag{23}$$

together with the boundary conditions

$$X = 0: \qquad [A_M] = 1 \tag{24}$$

$$X = 1: \qquad [A_M] = 0 \tag{25}$$

This case can be regarded as a limiting case of a general second-order reaction that is analogous to the case of the pseudo-first-order reaction in the liquid film in reactive absorption. The corresponding expression for the enhancement factor E_{1M}^∞ valid for high values of the Hatta number has been derived and published in paper [27] as follows:

$$E_{1M}^\infty = 0.729 \times Ha_M^{2/3} \tag{26}$$

1.3 Counter-current dialyzer with chemical reaction in stripping solution

A simple mathematical model of a counter-current dialyzer of rectangular cross-section is based on the assumption of a constant volumetric flow rate and plug flow of liquid in

each compartment with negligible solvent flux and ultrafiltration through the membrane. The assumption of plug flow in this type of equipment was proved in earlier study by Palatý and Žáková [28]. The balance scheme of a counter-current dialyzer in case of transport of a single solute (component A) through the membrane from compartment I to compartment II is depicted in Fig. 1.
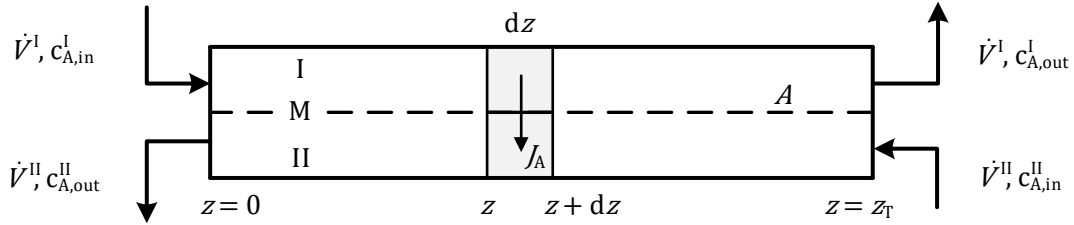

Fig. 1: Balance scheme of counter-current dialyzer

The differential mass balance of the transported component in both compartments can be derived as follows:

$$\frac{dc_A^I}{dz} = -J_A \frac{A}{\dot{V}^I z_T} \qquad \frac{dc_A^{II}}{dz} = -J_A \frac{A}{\dot{V}^{II} z_T} \qquad (27a,b)$$

where c_A^j is the molar concentration of component A and $\dot{V}^j$ is the volumetric flow rate of liquid in the respective compartment (j = I, II), z is the spatial coordinate, J_A is the molar flux of component A through the membrane, A is the membrane area and z_T is the height of the compartment. The simplest way to express the molar flux of component A is based on the overall dialysis coefficient K_A as follows:

$$J_A = K_A(c_A^I - c_A^{II}) \qquad (28)$$

For the transport of solute A, the extraction ratio ε can be defined as

$$\varepsilon = \frac{c_{A,in}^I - c_{A,out}^I}{c_{A,in}^I - c_{A,in}^{II}} \qquad (29)$$

The extraction ratio represents the actual achieved concentration change of component A in the feed solution as a fraction of the maximum attainable concentration change. If the fresh stripping solution is free of component A ($c_{A,in}^{II} = 0$), the extraction ratio becomes identical with the recovery fraction of component A from the feed. The expression for the extraction ratio for a counter-current dialyzer can be derived as [29]

$$\varepsilon = \frac{1 - e^{-N_t(1-Z)}}{1 - Z\, e^{-N_t(1-Z)}} \qquad (30)$$

where $N_t = K_A A / \dot{V}^I$ is the dimensionless parameter referred to as the number of transfer units and $Z = \dot{V}^I / \dot{V}^{II}$ is the flow ratio. For $Z = 1$ (i.e., $\dot{V}^I = \dot{V}^{II}$) and $Z \to 0$ (i.e., $\dot{V}^{II} \gg \dot{V}^I$), Eq. (30) reduces to

$$Z = 1: \quad \varepsilon = \frac{N_t}{N_t + 1} \qquad\qquad Z \to 0: \quad \varepsilon = 1 - e^{-N_t} \qquad (31a,b)$$

The extraction ratio of the transported component can be enhanced in the presence of a chemical reaction that occurs in the stripping solution. Due to the chemical reaction, the concentration of the transported solute can be significantly reduced in the stripping solution, hence increasing the driving force. An analytical expression for the extraction ratio can only be derived for the limiting case of an instantaneous irreversible reaction at an excess of reactive component B in the stripping solution. In this case, the concentration of the transported solute is maintained at zero at the membrane boundary at the stripping side of the membrane. This effect leads not only to maximizing the concentration difference between the solutions in both compartments but also to the elimination of the mass transfer resistance located in the liquid film adjacent to the membrane in compartment II. Hence, this case represents the maximum possible enhancement in the solute flux compared to the case of an infinitely slow reaction or the absence of the reactive component in the stripping solution. The molar flux of component A can be expressed as follows:

$$J_A^\infty = K_A^\infty c_A^I \tag{32}$$

where K_A^∞ is the overall dialysis coefficient, in which the mass transfer resistance in the liquid film in compartment II is neglected. Inserting Eq. (32) into Eq. (27a) and integrating along the dialyzer height yields

$$c_{A,out}^I = c_{A,in}^I \exp\left(-\frac{K_A^\infty A}{\dot{V}^I}\right) \tag{33}$$

Inserting Eq. (33) into the definition of the extraction ratio given by Eq. (29) results in the expression

$$\varepsilon^\infty = 1 - e^{-N_t^\infty} \tag{34}$$

Eq. (34) for the extraction ratio in the case of an instantaneous irreversible reaction at an excess of reactive component B in the stripping solution is formally identical with Eq. (31b) for the extraction ratio in the case of absence of a chemical reaction for the value of parameter $Z = 0$.

2. Aims of the doctoral dissertation

2.1 Absorption accompanied by irreversible second-order reaction

The mathematical model of absorption accompanied by an irreversible second-order reaction $A + \nu_B B \to \nu_P P$ is based on the differential mass balance of reacting components A and B in the dimensionless forms (5) and (6) with the corresponding boundary conditions (8a,b) and (9a,b). Unfortunately, analytical solution of this problem is not available except for several limiting cases. A number of approximate analytical solutions for the enhancement factor for an irreversible second-order reaction have been published – these are listed in Tab. 1. However, the literature review has revealed that a detailed critical comparison of these approximate solutions had not been provided yet.

In the first part of the doctoral dissertation, the exact numerical solution of Eqs (5) and (6) with boundary conditions (8a,b) and (9a,b) is to be provided for a wide and finely discretized range of parameters Ha and E_2^∞. The approximate solutions for the

enhancement factor presented in Tab. 1 are then to be compared with the results obtained by this numerical solution and the accuracy of the approximate solutions is to be evaluated. Based on this evaluation, modifications of the existing approximate solutions might also be proposed that would result in accuracy improvement.

2.2 Dialysis accompanied by irreversible second-order reaction in membrane

The mathematical model of dialysis accompanied by an irreversible second-order reaction $A + \nu_B B \rightarrow \nu_P P$ that takes place in the membrane is based on the differential mass balance of reacting components A and B in the dimensionless forms (18) and (19) with the corresponding boundary conditions (21a,b) and (22a,b). Unfortunately, analytical solution of this problem is not available except for several limiting cases. One of the limiting cases is characterized by linear concentration profile of reactive component B in the membrane. The corresponding differential mass balance of component A in the dimensionless form is given by Eq. (23) with boundary conditions (24) and (25). For this case, analytical expression (26) for the enhancement factor has been derived that is only valid for high values of the Hatta number [27]. As a starting point of the numerical analysis of dialysis accompanied by a second-order reaction in the membrane, this limiting case is to be investigated based on the numerical solution of Eq. (23) with boundary conditions (24) and (25) and the expression for the enhancement factor E_{1M} valid for a complete range of the Hatta number Ha_M is to be developed.

In the next step, the exact numerical solution of Eqs (18) and (19) with boundary conditions (21a,b) and (22a,b) is to be provided for a wide and finely discretized range of parameters Ha_M and E_{2M}^{∞} and the effect of a chemical reaction on the rate of dialysis is to be evaluated in terms of the enhancement factor E_{2M}. The results obtained by this numerical solution are then to be used for a development of the approximate analytical solution for the enhancement factor E_{2M} in the form $E_{2M} = f(Ha_M, E_{2M}^{\infty})$.

2.3 Counter-current dialyzer with chemical reaction in stripping solution

A simple model of a counter-current dialyzer is based on the differential mass balance of the transported component in both dialyzer compartments given by Eqs (27a,b). A second-order reaction $A + B \rightleftharpoons P$ of transported component A is to be considered in the stripping solution with reactive component B (both irreversible and reversible). Both reactive component B and reaction product P are present solely in the stripping solution and cannot pass through the membrane. In order to account for the chemical reaction in the stripping solution, Eq. (27b) has to be extended to include the reaction term and balance equations for other components involved in the chemical reaction in the stripping solution have to be added to Eqs (27a,b). Instead of relying on Eq. (28) to determine the flux of component A from compartment I to compartment II, transport of component A in the membrane and liquid films has to be treated rigorously.

Based on these considerations, a mathematical model of a counter-current dialyzer with a chemical reaction in the stripping solution is to be elaborated and employed to evaluate the effect of several key parameters (flow ratio, inlet concentration of reactive component B, reaction rate constant, equilibrium constant) on the extraction ratio of transported component A in the dialyzer.

3. Methods

3.1 Absorption accompanied by irreversible second-order reaction

The mathematical model of absorption accompanied by an irreversible second-order reaction represents a boundary value problem for a system of two second-order ordinary differential equations (5) and (6) with boundary conditions (8a,b) and (9a,b). As no analytical solution exists for this problem, the set of Eqs (5) and (6) has to be solved by means of an appropriate numerical method. De Santiago and Farina [18] presented a numerical solution strategy for the set of Eqs (5) and (6), in which both equations are combined into the single second-order equation

$$\frac{d^2[B]}{dX^2} - \frac{1}{E_2^\infty - 1}\frac{d^2[A]}{dX^2} = 0 \tag{35}$$

and integrated with boundary conditions

$$X = 0: \qquad \frac{d[A]}{dX} = -E_2 \qquad \frac{d[B]}{dX} = 0 \tag{36a,b}$$

$$X = 1: \qquad [A] = 0 \qquad [B] = 1 \tag{37a,b}$$

resulting in the expression for the dimensionless relative concentration of component B

$$[B] = \frac{[A]}{E_2^\infty - 1} - \frac{E_2}{E_2^\infty - 1}(1 - X) + 1 \tag{38}$$

Eq. (38) is finally substituted into Eq. (5), resulting in the final second-order differential equation

$$\frac{d^2[A]}{dX^2} = Ha^2[A]\left\{\frac{[A]}{E_2^\infty - 1} - \frac{E_2}{E_2^\infty - 1}(1 - X) + 1\right\} \tag{39}$$

Prior to numerical treatment, Eq. (39) must be transformed into a system of two first-order equations. This system of equations can then be solved using the Runge–Kutta fourth-order method. For Eq. (39), the following initial conditions shall be considered:

$$X = 0: \qquad [A] = 1 \qquad \frac{d[A]}{dX} = -E_2 \tag{40a,b}$$

As the value of the enhancement factor E_2 in Eq. (39), as well as in boundary condition (40b) is essentially unknown, Eq. (39) has to be solved by the shooting method, i.e., the procedure searching for such value of E_2 that satisfies the boundary condition (9a) for $[A]$.

The numerical scheme developed was implemented in the object-oriented computer programming language. The computer code was written in the Object Pascal language implemented in Borland Delphi© Professional. The accuracy of the numerical solution was enhanced by using non-uniform integration steps and Richardson extrapolation. The calculation of the values of the enhancement factor E_2 has been carried out for 12 753 combinations of parameters Ha and E_2^∞. The values of E_2^∞ ranged from 1.1 to 1000,

14

while those of Ha ranged from 0.1 to $m \times Ha$ ($m = 10$, 20 and 50 for the values of E_2^∞ up to 2, from 2 to 10 and above 10, respectively). Both Ha and E_2^∞ were approximately evenly spaced on a logarithmic scale within the indicated ranges.

3.2 Dialysis accompanied by irreversible second-order reaction in membrane

The mathematical model of dialysis accompanied by an irreversible second-order reaction that takes place in the membrane for the limiting case of linear concentration profile of reactive component B represents a boundary value problem for a single second-order ordinary differential equation (23) with boundary conditions (24) and (25). For a general case of an irreversible second-order reaction, Eqs (18) and (19) have to be considered together with boundary conditions (21a,b) and (22a,b) that represent a boundary value problem for a system of two second-order ordinary differential equations.

As no analytical solution exists for these problems, an appropriate numerical method has to be used. While a numerical solution strategy based on the shooting method was used for the mathematical model of absorption accompanied by an irreversible second-order reaction, here, the finite difference method was used that is based on the discretization of differential equations using a set of grid points generated along the problem's domain (interval bounded by points at which boundary conditions are provided). At each grid point, the derivatives in differential equations are approximated by suitable finite difference formulas. In this way, differential equations can be converted into a system of algebraic equations that can be solved by matrix algebra techniques.

Efficient numerical schemes based on the finite difference method were elaborated for Eq. (23) with boundary conditions (24) and (25) and for Eqs (18) and (19) with boundary conditions (21a,b) and (22a,b). The numerical schemes developed were implemented in the object-oriented computer programming language. The computer code was written in the Object Pascal language implemented in Borland Delphi© Professional. The accuracy of the numerical solution was enhanced by using non-uniform discretization steps and Richardson extrapolation. The calculation of the values of the enhancement factor E_{1M} was carried out for 501 values of parameter Ha_M from 0.1 to 10 000 that were evenly spaced on a logarithmic scale within the indicated range. The calculation of the values of the enhancement factor E_{2M} was carried out for 16 243 combinations of parameters Ha_M and E_{2M}^∞. The values of E_{2M}^∞ ranged from 1.1 to 1000, while those of Ha_M ranged from 0.1 to $80 \times (E_{2M}^\infty)^{3/2}$. The upper limit of Ha_M was chosen that is approximately ten times higher than the value of Ha_M that corresponds to the limiting case of an instantaneous reaction. Both Ha_M and E_{2M}^∞ were approximately evenly spaced on a logarithmic scale within the indicated ranges.

3.3 Counter-current dialyzer with chemical reaction in stripping solution

A counter-current dialyzer of rectangular cross-section with the identical compartments I and II is depicted in Fig. 2. The transport of a single solute (component A) is assumed through the membrane from compartment I to compartment II, where a second-order reaction $A + B \rightleftharpoons P$ takes place.
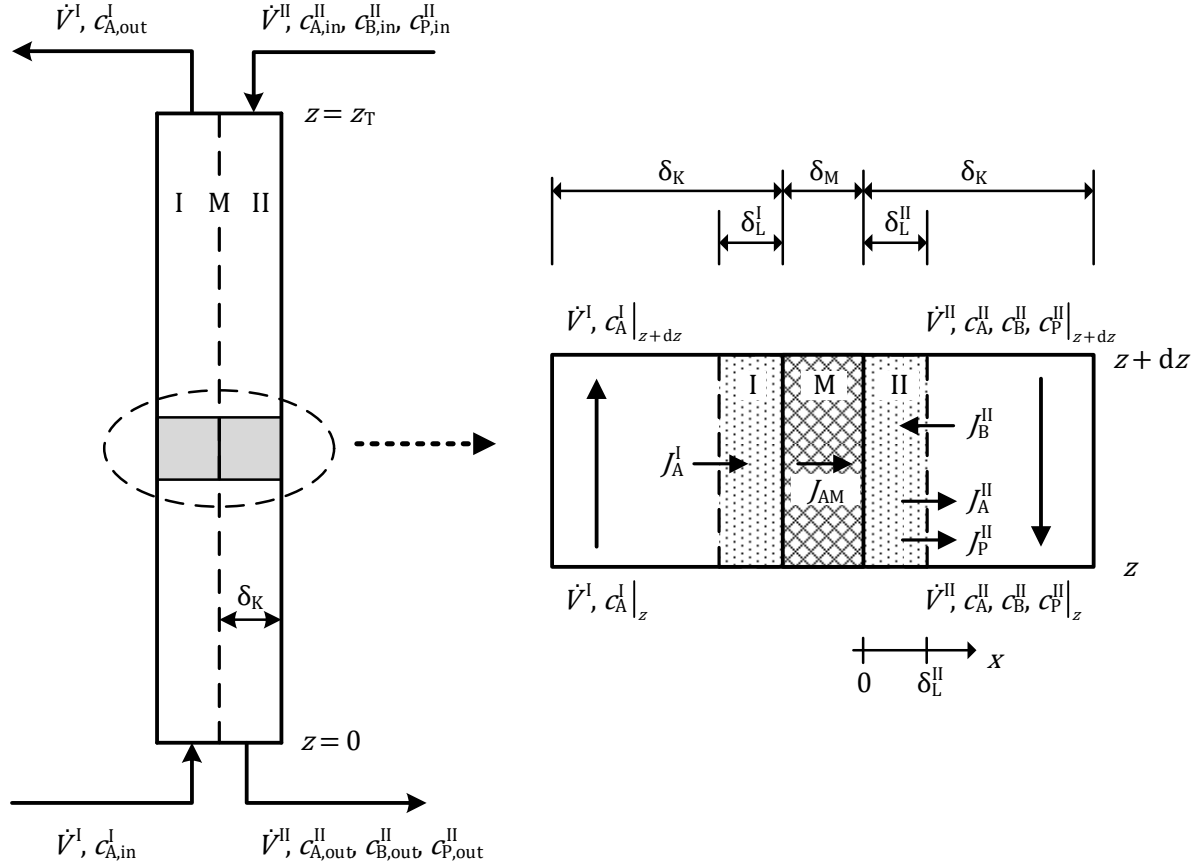
Fig. 2: Balance scheme of counter-current dialyzer with chemical reaction in stripping solution

The steady-state differential mass balance of components A, B and P in compartments I and II can be derived as follows:

$$\frac{dc_A^I}{dz} = -J_A^I \frac{A}{\dot{V}^I z_T} \tag{41}$$

$$\frac{dc_A^{II}}{dz} = -J_A^{II} \frac{A}{\dot{V}^{II} z_T} + \frac{k_2 S}{\dot{V}^{II}} \left(c_A^{II} c_B^{II} - \frac{c_P^{II}}{K_c} \right) \left(1 - \frac{A}{S z_T} \delta_L^{II} \right) \tag{42}$$

$$\frac{dc_B^{II}}{dz} = J_B^{II} \frac{A}{\dot{V}^{II} z_T} + \frac{k_2 S}{\dot{V}^{II}} \left(c_A^{II} c_B^{II} - \frac{c_P^{II}}{K_c} \right) \left(1 - \frac{A}{S z_T} \delta_L^{II} \right) \tag{43}$$

$$\frac{dc_P^{II}}{dz} = -J_P^{II} \frac{A}{\dot{V}^{II} z_T} - \frac{k_2 S}{\dot{V}^{II}} \left(c_A^{II} c_B^{II} - \frac{c_P^{II}}{K_c} \right) \left(1 - \frac{A}{S z_T} \delta_L^{II} \right) \tag{44}$$

In Eqs (41)–(44), c_i^j is the molar concentration and J_i^j is the molar flux of the respective component related to the liquid bulk in the respective compartment (i = A, B, P; j = I, II), z is the spatial coordinate, A is the membrane area, $\dot{V}^j$ is the volumetric flow rate of liquid in the respective compartment (j = I, II), S is the cross-section of each compartment, z_T is the height of the compartment, k_2 is the second-order reaction rate constant, K_c is the equilibrium constant and δ_L^{II} is the thickness of the liquid film in compartment II.

The boundary conditions for Eqs (41)–(44) are

$$z = 0: \qquad c_A^I = c_{A,in}^I \tag{45}$$

$$z = z_T: \qquad c_A^{II} = 0 \qquad c_B^{II} = c_{B,in}^{II} \qquad c_P^{II} = 0 \tag{46a,b,c}$$

In order to calculate the fluxes $J_A^I, J_A^{II}, J_B^{II}$ and J_P^{II}, it is necessary to solve mass transfer in the membrane and in the liquid films simultaneously. The fluxes of component A in the liquid film in compartment I and in the membrane can be expressed as follows:

$$J_A^I = k_L^I\left(c_A^I - c_{Ai}^I\right) \qquad J_{AM} = \frac{D_{AM}}{\delta_M}\left(c_{AM}^I - c_{AM}^{II}\right) \tag{47a,b}$$

where c_{Ai}^I and c_{AM}^j (j = I, II) are the concentrations of component A in liquid at the solution/membrane interface at the feed side and in the membrane at both boundaries, respectively, k_L^I is the mass transfer coefficient in the liquid film in compartment I, D_{AM} is the diffusion coefficient of component A in the membrane and δ_M is the thickness of the membrane. The transport of components A, B and P in the liquid film in compartment II must be solved simultaneously due to the existence of a chemical reaction between the components. The differential mass balance can be formulated for the reacting components in the liquid film as follows:

$$D_A^{II}\frac{d^2 c_A^f}{dx^2} - k_2\left(c_A^f c_B^f - \frac{c_P^f}{K_c}\right) = 0 \tag{48}$$

$$D_B^{II}\frac{d^2 c_B^f}{dx^2} - k_2\left(c_A^f c_B^f - \frac{c_P^f}{K_c}\right) = 0 \tag{49}$$

$$D_P^{II}\frac{d^2 c_P^f}{dx^2} + k_2\left(c_A^f c_B^f - \frac{c_P^f}{K_c}\right) = 0 \tag{50}$$

In Eqs (48)–(50), D_i^{II} is the diffusion coefficient and c_i^f is the molar concentration of the respective component in the liquid film in compartment II (i = A, B, P).

The boundary conditions for Eqs (48)–(50) are

$$x = 0: \qquad c_A^f = c_{Ai}^{II} \qquad \frac{dc_B^f}{dx} = 0 \qquad \frac{dc_P^f}{dx} = 0 \tag{51a,b,c}$$

$$x = \delta_L^{II}: \qquad c_A^f = c_A^{II} \qquad c_B^f = c_B^{II} \qquad c_P^f = c_P^{II} \tag{52a,b,c}$$

The mass transfer coefficient k_L^I in Eq. (47a) and the thickness of the liquid film δ_L^{II} in Eqs (42)–(44) can be estimated from the well-established empirical correlation [30]

$$Sh = C Re^{0.5} Sc^{0.33} \tag{53}$$

where Sh is the Sherwood number, C is a constant, Re is the Reynolds number and Sc is the Schmidt number. The equilibrium relations (54) must be added to the set of Eqs (47)–(53)

$$c_{AM}^j = \Psi_A^j c_{Ai}^j \qquad (j = I, II) \tag{54}$$

where Ψ_A^j is the partition coefficient of component A between the membrane and liquid in the individual compartments (j = I, II). At steady state, the flux of component A in the liquid film in compartment I is equal to those in the membrane and in the liquid film in compartment II at the solution/membrane interface:

$$J_A^{I} = J_{AM} = -D_A^{II} \frac{dc_A^f}{dx}\bigg|_{x=0} \tag{55}$$

The mathematical model of a counter-current dialyzer with a chemical reaction in the stripping solution based on the set of differential equations (41)–(44) with boundary conditions (45) and (46a,b,c) represents a boundary value problem that can only be solved numerically by means of an appropriate numerical method. The solution procedure based on the shooting method was proposed as follows:

1. The initial estimate of the concentration of component A in the stream leaving compartment I ($c_{A,out}^{I}$) was provided. The boundary condition (45) was replaced with the modified boundary condition (56) based on this estimate, thus reducing the boundary value problem to the initial value problem:

$$z = z_T: \qquad c_A^I = c_{A,out}^I \tag{56}$$

2. The set of differential equations (41)–(44) was integrated from $z = z_T$ to $z = 0$ for the initial conditions (46a,b,c) and (56) using the Runge–Kutta fourth-order method.

3. The procedure was repeated until the boundary condition (45) was satisfied with the accuracy of 1×10^{-8} %. The bisection method was used to find the value of $c_{A,out}^I$, which would satisfy the boundary condition (45).

In each elementary step of the Runge–Kutta method, it was necessary to determine the fluxes J_A^I, J_A^{II}, J_B^{II} and J_P^{II} based on the concentration profiles of all components obtained by numerical solution of the system of Eqs (47a,b)–(55). The finite difference method was used to solve differential equations (48)–(50) with boundary conditions (51a,b,c) and (52a,b,c).

The mathematical model represented by the set of differential equations (41)–(44) and (48)–(50) is applicable to the case of a reversible second-order reaction A + B ⇌ P. For an irreversible second-order reaction A + B → P, Eqs (44) and (50) for component P can be omitted together with the terms c_P^{II}/K_c and c_P^f/K_c in Eqs (42) and (43) and Eqs (48) and (49), respectively. The concentration of component P does not influence the flux of component A from compartment I to compartment II and it can be determined by a simple material balance in the stripping solution leaving the dialyzer, as well as in any cross-section of the dialyzer.

The numerical scheme developed was implemented in the object-oriented computer programming language. The computer code was written in the Object Pascal language implemented in Borland Delphi[©] Professional. The complete list of the variables used in numerical treatment is summarized in Tab. 2.

Tab. 2: List of specified variables used in numerical treatment

Variable	Value or range	Unit
A	3.31×10^{-2}	m^2
S	3.96×10^{-5}	m^2
z_T	0.92	m
δ_M	165×10^{-6}	m
$c_{A,in}^I$	$1 \times 10^{-3} - 1$	$kmol\ m^{-3}$
$c_{A,in}^{II}, c_{P,in}^{II}$	0	$kmol\ m^{-3}$
$c_{B,in}^{II}$	$0 - 2$	$kmol\ m^{-3}$
$D_A^I, D_A^{II}, D_B^{II}, D_P^{II}$	1×10^{-9}	$m^2\ s^{-1}$
D_{AM}	$1 \times 10^{-12} - 1 \times 10^{-9}$	$m^2\ s^{-1}$
Ψ_A^I, Ψ_A^{II}	1	$-$
μ	1×10^{-3}	$Pa\ s$
ρ	1000	$kg\ m^{-3}$
$\dot{V}^I, \dot{V}^{II}$	$5 \times 10^{-9} - 30 \times 10^{-9}$	$m^3\ s^{-1}$
k_2	$1 \times 10^{-4} - 10$	$m^3\ kmol^{-1}\ s^{-1}$
K_c	$0.1 - 1000$	$m^3\ kmol^{-1}$
C	1	$-$

4. Results and discussion

4.1 Absorption accompanied by irreversible second-order reaction

The maximum relative deviations of the approximate analytical solutions for the enhancement factor for an irreversible second-order reaction $A + \nu_B B \rightarrow \nu_P P$ from the results of the exact numerical solution are summarized in Tab. 3. From Tab. 3, it is evident that all approximate solutions are able to predict the values of the enhancement factor with the relative deviations within 10 % compared to the exact numerical solution for the film theory. The maximum relative deviation of the approximate solution of van Krevelen and Hoftijzer [14] was found to be less than 3 %. This conclusion is in complete agreement with earlier communication of de Santiago and Farina [18] and Wellek et al. [22]. Despite being the oldest one, the approximate solution of van Krevelen and Hoftijzer was proved to be the most accurate existing approximate solution for the enhancement factor for an irreversible second-order reaction applicable for the entire range of parameters Ha and E_2^∞. However, the main disadvantage of this approximate solution is its implicit nature.

Tab. 3: Maximum relative deviations of approximate analytical solutions

Author	Maximum relative deviation (%)	
	Negative	**Positive**
van Krevelen and Hoftijzer (1948)	−2.8	–
Hikita and Asai (1964)	−1.9	+6.3
Porter (1966)	−3.6	+6.3
Yeramian et al. (1970)	−6.6	–
de Santiago and Farina (1970)	−2.7	–
Kishinevskii et al. (1971)	−2.0	+8.7
DeCoursey (1974)	−1.8	+8.8
Baldi and Sicardi (1975)	–	+9.6
Wellek et al. (1978)	−5.6	+4.1
Karlsson and Bjerle (1980)	−8.2	+5.0
Last and Stichlmair (2002)	−4.8	+5.4

The approximate solution of Wellek et al. [22] represents an empirical correlation that was derived on the basis of the asymptotic behavior of the function $E_2 = f(Ha, E_2^\infty)$ in the form

$$\left(\frac{1}{E_2 - 1}\right)^n = \left(\frac{1}{E_2^\infty - 1}\right)^n + \left(\frac{1}{E_1 - 1}\right)^n \qquad (57)$$

Using the original value of the adjustable parameter ($n = 1.35$), the relative deviations of the approximate solution from the results of the exact numerical solution were found within 5.6 %. Based on the fitting of Eq. (57) to the results of the exact numerical solution for 12 753 combinations of parameters Ha and E_2^∞, the optimum value of $n = 1.383$ was found that results in the maximum relative deviation of 4.7 %.

The relative deviations of the approximate solution of DeCoursey [20] derived on the basis of the surface renewal theory from the results of the exact numerical solution for the film theory can be as high as 8.8 %. However, it was found that the peak in the relative deviation is basically due to the difference between both theories. A correction factor to the original approximate solution of DeCoursey was proposed as follows:

$$F = 1 + \{1 - \exp[-0.4 \times (E_2^\infty - 1)]\} \times \left(\frac{Ha}{\sqrt{1 + Ha^2}\tanh Ha} - 1\right) \qquad (58)$$

If the right-hand side of the expression for the enhancement factor is multiplied by the correction factor (58), the maximum relative deviation becomes as low as 2.2 %. This modification of the existing approximate solution of DeCoursey results in the best accuracy that has ever been reported for any explicit approximate solution for the enhancement factor for an irreversible second-order reaction.

4.2   Dialysis accompanied by irreversible second-order reaction in membrane

Based on numerical solution of Eq. (23) with the corresponding boundary conditions (24) and (25), the validity of Eq. (26) for high values of the Hatta number has been confirmed. For $Ha_M > 4$ and $Ha_M > 6$, the relative deviation of Eq. (26) from the results of the numerical solution is less than 1 % and 0.1 %, respectively, but it dramatically rises for lower values of the Hatta number. In order to obtain the expression for E_{1M} valid for a wide range of the Hatta number, Eq. (26) was extended in order to account for the condition $\lim_{Ha_M \to 0} E_{1M} = 1$ as follows:

$$E_{1M} = [1 + (E_{1M}^\infty)^n]^{1/n} = \left[1 + \left(0.729 \times Ha_M^{2/3}\right)^n\right]^{1/n} \tag{59}$$

In Eq. (59), the parameter n was adjusted in order to minimize the deviation of the expression compared to the numerical solution for the entire range of the Hatta number under the study (0.1 to 10 000). For $n = 4$, the relative deviation of Eq. (59) was found within 1.5 % compared to the numerical solution. Eq. (59) can then be rewritten as

$$E_{1M} = \sqrt[4]{1 + 0.282 \times Ha_M^{8/3}} \tag{60}$$

The mathematical model of dialysis accompanied by an irreversible second-order reaction $A + \nu_B B \to \nu_P P$ that takes place in the membrane is represented by Eqs (18) and (19) with boundary conditions (21a,b) and (22a,b). Graphical representation of the results of the numerical solution of this model is provided in Fig. 3 that shows the enhancement factor E_{2M} as a function of the Hatta number Ha_M with the enhancement factor corresponding to an instantaneous reaction E_{2M}^∞ as a parameter.
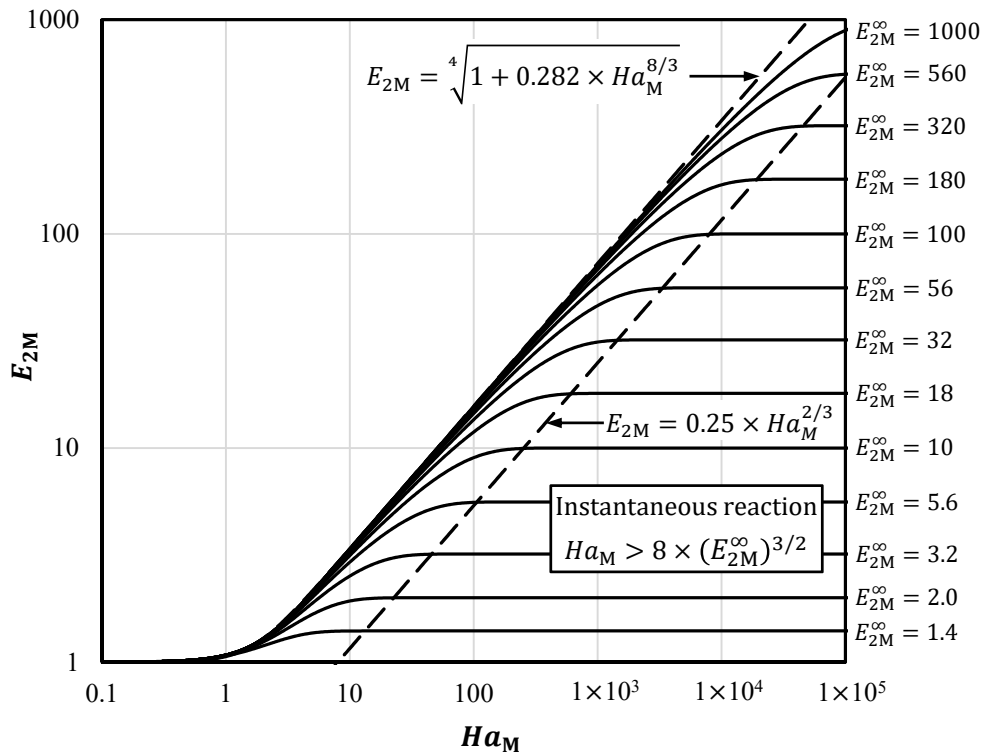

Fig. 3: Enhancement factor for dialysis accompanied by irreversible second-order reaction in membrane

The asymptotic behavior of the function $E_{2M} = f(Ha_M, E_{2M}^\infty)$ for high and low values of Ha_M is apparent from Fig. 3. For $Ha_M > 8 \times (E_{2M}^\infty)^{3/2}$, the relative deviation of the enhancement factor E_{2M} from the enhancement factor E_{2M}^∞ corresponding to an instantaneous irreversible second-order reaction given by Eq. (20b) is always lower than 1 %.

In order to develop a general correlation (approximate analytical solution) for the enhancement factor E_{2M}, two expressions were proposed that were based on the analogy with the approximate analytical solutions for the enhancement factor for absorption accompanied by an irreversible second-order reaction. The first expression is based on the general form of the approximate solution of Wellek et al. [22]:

$$\left(\frac{1}{E_{2M} - 1}\right)^n = \left(\frac{1}{E_{2M}^\infty - 1}\right)^n + \left(\frac{1}{E_{1M} - 1}\right)^n \tag{61}$$

The latter expression is based on Eq. (60), in which the Hatta number is multiplied by an auxiliary factor containing the enhancement factor.

$$E_{2M} = \sqrt[4]{1 + 0.282 \times Ha_M^{8/3} \left(\frac{E_{2M}^\infty - E_{2M}}{E_{2M}^\infty - 1}\right)^n} \tag{62}$$

In Eqs (61) and (62), the parameter n was adjusted in order to minimize the deviation of the respective expression compared to the numerical solution for 16 243 combinations of parameters Ha_M and E_{2M}^∞. For Eq. (61), the best agreement was found for $n = 1.95$ (maximum relative deviation of 6.8 %). For Eq. (62), the best agreement was found for $n = 1.025$ (maximum relative deviation of 1.5 %). However, for $n = 1.000$, Eq. (62) becomes a quartic equation

$$E_{2M}^4 + \frac{0.282 \times Ha_M^{8/3}}{E_{2M}^\infty - 1} E_{2M} - \left(1 + \frac{0.282 \times Ha_M^{8/3}}{E_{2M}^\infty - 1} E_{2M}^\infty\right) = 0 \tag{63}$$

The relative deviation of Eq. (63) was found within 2 % compared to the numerical solution for the entire range of parameters Ha_M and E_{2M}^∞ under the study. According to the Descartes rule of signs, Eq. (63) has one positive and one negative root. Only the positive root has a meaning, and therefore, represents the enhancement factor. Analytical solution of quartic equation (63) is possible, though somewhat laborious. Therefore, numerical solution of Eq. (63) is also an alternative. Among various numerical methods, especially the Newton's method is favorable due to its rapid convergence for any initial guess E_2^* ($1 < E_2^* < E_2^\infty$).

4.3 Counter-current dialyzer with chemical reaction in stripping solution

The effect of the inlet concentration of reactive component B in the stripping solution on the extraction ratio of component A for dialysis accompanied by an instantaneous irreversible reaction in the stripping solution is presented in Fig. 4a for several values of the flow ratio ($Z = 0.5$, 1, 2) and membrane diffusion coefficient ($D_{AM} = 4\times10^{-11}$, 5×10^{-10} m^2 s^{-1}). The points F_i and G_i ($i = 1, 2, 3$) correspond to the absence of

component B, while the points F_∞ and G_∞ correspond to an excess of component B in the stripping solution.
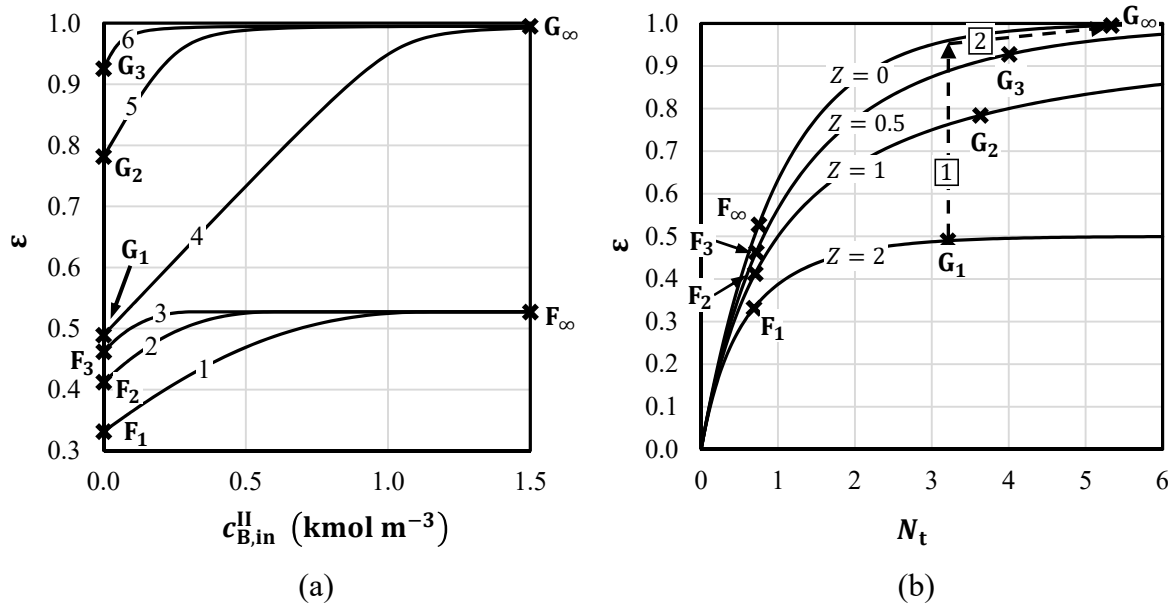

(a)

(b)

Fig. 4: Extraction ratio of component A: (a) dependence upon inlet concentration of reactive component B in stripping solution for instantaneous irreversible reaction: $c_{A,in}^I = 1$ kmol m^{-3}, $\dot{V}^I = 10\times10^{-9}$ m^3 s^{-1}, D_{AM} (m^2 s^{-1}) / $\dot{V}^{II}$ (m^3 s^{-1}): (1) 4×10^{-11} / 5×10^{-9} ($Z = 2$), (2) 4×10^{-11} / 10×10^{-9} ($Z = 1$), (3) 4×10^{-11} / 20×10^{-9} ($Z = 0.5$), (4) 5×10^{-10} / 5×10^{-9} ($Z = 2$), (5) 5×10^{-10} / 10×10^{-9} ($Z = 1$), (6) 5×10^{-10} / 20×10^{-9} ($Z = 0.5$); (b) as function of number of transfer units according to Eqs (30) and (31a,b)

The points F_i and G_i ($i = 1, 2, 3, \infty$) are also plotted in Fig. 4b, where the extraction ratio is shown as a function of parameter $N_t = K_A A/\dot{V}^I$ (number of transfer units). The enhancement in the extraction ratio is represented by the vertical distance of points F_∞–F_i and G_∞–G_i ($i = 1, 2, 3$). The maximum enhancement is achieved due to the two factors: (1) maximizing the driving force by maintaining the membrane boundary at the stripping side at zero concentration of component A; (2) complete elimination of the mass transfer resistance located in the liquid film at the stripping side of the membrane. The first contribution can be viewed as the shift of the respective point in the ordinate direction towards the curve $\varepsilon = f(N_t)$ for $Z = 0$, while the latter contribution can be viewed as the further shift of the respective point along the curve $\varepsilon = f(N_t)$ for $Z = 0$ from N_t to N_t^∞.

Both the finite reaction rate constant and reaction reversibility adversely affect the actual enhancement in the extraction ratio compared to the case of an instantaneous irreversible reaction. Figs 5a and 6a show the dependence of the extraction ratio of component A on the inlet concentration of reactive component B for several values of the reaction rate constant k_2 and equilibrium constant K_c, respectively, as a parameter. From Figs 5a and 6a it is evident that the extraction ratio decreases with the decreasing value of the reaction rate constant and equilibrium constant, respectively. For slow or reversible reactions, the low value of the reaction rate constant and equilibrium constant can be compensated by a heavy excess of component B in compartment II as demonstrated in Figs 5b and 6b, respectively.
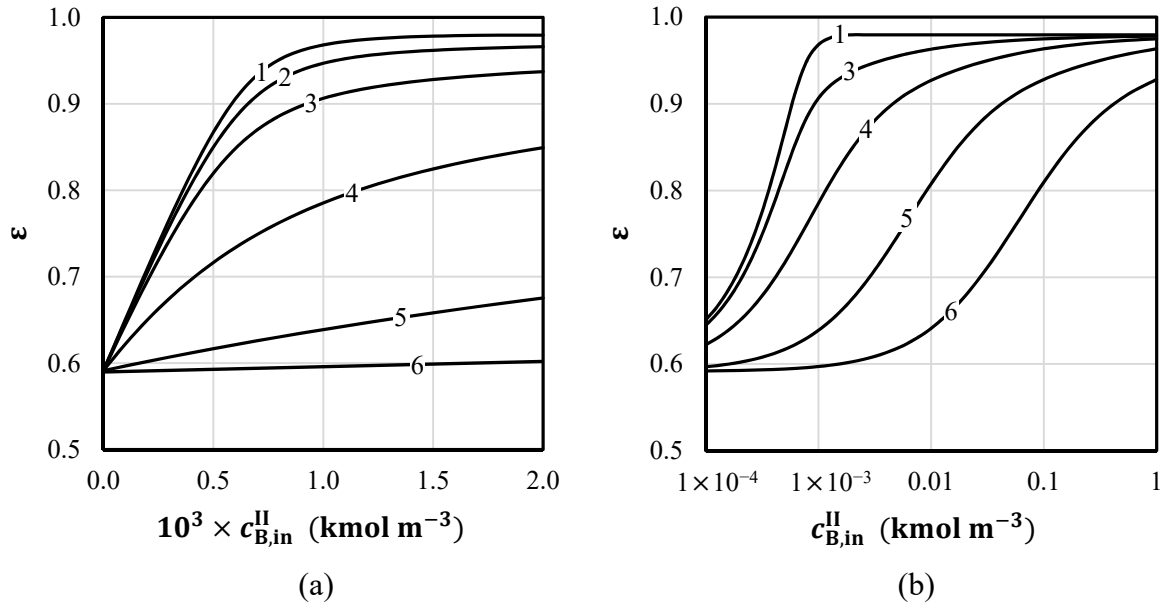
Fig. 5: Dependence of extraction ratio of component A upon inlet concentration of reactive component B in stripping solution for irreversible reaction of finite reaction rate constant: $c_{A,in}^{I} = 1 \times 10^{-3}$ kmol m^{-3}, $D_{AM} = 5 \times 10^{-10}$ m^2 s^{-1}, $\dot{V}^{I} = 15 \times 10^{-9}$ m^3 s^{-1}, $\dot{V}^{II} = 10 \times 10^{-9}$ m^3 s^{-1} ($Z = 1.5$), k_2 (m^3 kmol^{-1} s^{-1}): (1) instantaneous reaction ($k_2 \to \infty$), (2) 100, (3) 10, (4) 1, (5) 0.1, (6) 0.01; (a) comparable inlet concentrations of A and B; (b) excess of reactive component B in stripping solution
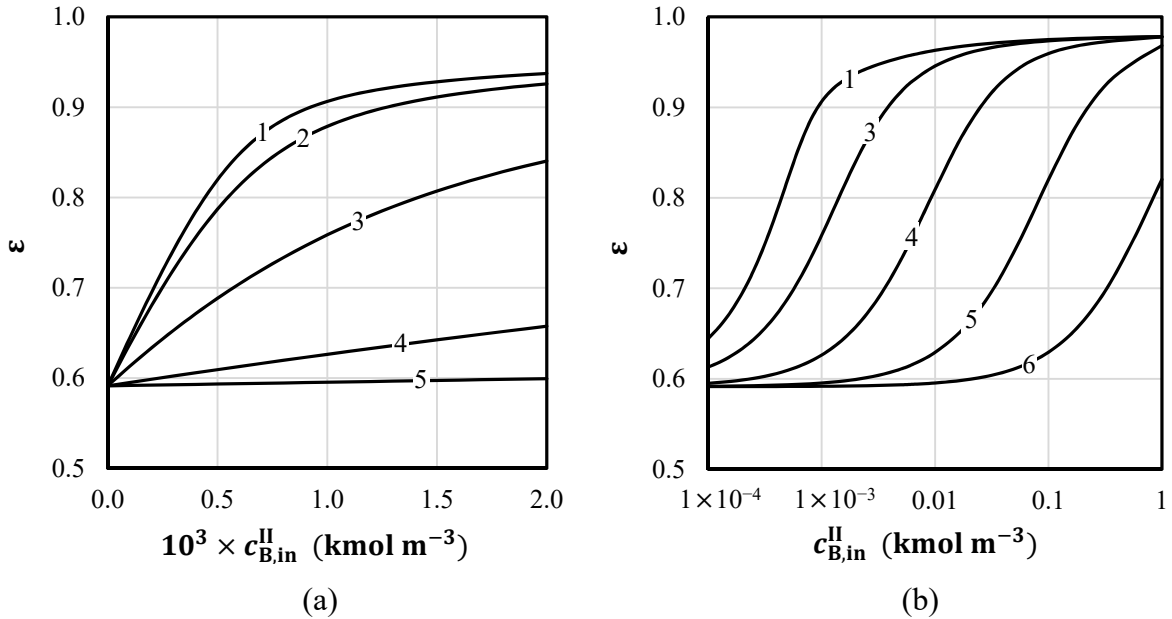

Fig. 6: Dependence of extraction ratio of component A upon inlet concentration of reactive component B in stripping solution for reversible reaction of finite reaction rate constant: $c_{A,in}^{I} = 1 \times 10^{-3}$ kmol m^{-3}, $D_{AM} = 5 \times 10^{-10}$ m^2 s^{-1}, $\dot{V}^{I} = 15 \times 10^{-9}$ m^3 s^{-1}, $\dot{V}^{II} = 10 \times 10^{-9}$ m^3 s^{-1} ($Z = 1.5$), $k_2 = 10$ m^3 kmol^{-1} s^{-1}, K_c (m^3 kmol^{-1}): (1) irreversible reaction ($K_c \to \infty$), (2) 10 000, (3) 1000, (4) 100, (5) 10, (6) 1; (a) comparable inlet concentrations of A and B; (b) excess of reactive component B in stripping solution

24

Conclusion

The existing approximate solutions for the enhancement factor for an irreversible second-order reaction were assessed based on the results of the exact numerical solution of the mathematical model of absorption accompanied by an irreversible second-order reaction based on the film theory. The maximum relative deviations of all approximate solutions did not exceed 10 %. The classical approximate solution of van Krevelen and Hoftijzer [14] has traditionally been considered the most accurate expression for the enhancement factor applicable for the entire range of parameters Ha and E_2^∞. The maximum relative deviation of this approximate solution of 2.8 % was confirmed but the implicit nature of this approximate solution makes its application difficult. A modification of the approximate solution of DeCoursey [20] originally based on the surface renewal theory was proposed by introducing a correction factor. The maximum relative deviation of this modified approximate solution was found to be within 2.2 % as compared to the exact numerical solution for the film theory, which is the best accuracy that has ever been reported for an explicit expression valid for the entire range of parameters Ha and E_2^∞.

Based on the mathematical model of dialysis accompanied by an irreversible second-order reaction that takes place in the membrane, the effect of a chemical reaction on the rate of dialysis was analyzed and evaluated in terms of the enhancement factor. As a part of the numerical analysis, limiting cases of dialysis accompanied by an irreversible second-order reaction were investigated, i.e., dialysis with instantaneous reaction and dialysis with linear concentration profile of reactive component B in the membrane. Two approximate solutions for the enhancement factor for dialysis accompanied by an irreversible second-order reaction were proposed. The first approximate solution was based on the approximate solution of Wellek et al. [22] for reactive absorption and its maximum relative deviation from the exact analytical solution was found within 6.8 %. The latter approximate solution was derived in the form of the quartic equation and its maximum relative deviation from the exact analytical solution did not exceed 2 % for the entire range of parameters Ha_M and $E_{2\mathrm{M}}^\infty$ under the study.

The mathematical model of a continuous counter-current dialyzer with a second-order chemical reaction in the stripping solution, both irreversible and reversible, was developed and used to evaluate the effect of the chemical reaction in the stripping solution on the performance of the dialyzer in terms of the extraction ratio of the transported component. The maximum enhancement in the extraction ratio was observed for the instantaneous irreversible reaction with an excess of the reactive component in the stripping solution. Both the finite reaction rate constant and reaction reversibility can adversely influence the enhancement in the extraction ratio. In certain cases, these effects can be compensated by a heavy excess of the reactive component in the stripping solution.

List of references

[1] KLEIN, E., SMITH, J. K., WENDT, R. P., DESAI, S. V. Solute separations from water by dialysis. I. The separation of aniline. *Separ. Sci.* 1972, **7-3**, 285–292.

[2] KLEIN, E., SMITH, J. K., WEAVER, R. E. C., WENDT, R. P., DESAI, S. V. Solute separations from water by dialysis. II. The separation of phenol by downstream conjugation. *Separ. Sci.* 1973, **8-5**, 585–592.

[3] HAN, S., FERREIRA, F. C., LIVINGSTON, A. Membrane aromatic recovery system (MARS) – a new membrane process for the recovery of phenols from wastewaters. *J. Membr. Sci.* 2001, **188**, 219–233.

[4] FERREIRA, F. C., HAN, S., LIVINGSTON, A. G. Recovery of aniline from aqueous solution using the membrane aromatic recovery system (MARS). *Ind. Eng. Chem. Res.* 2002, **41**, 2766–2774.

[5] FERREIRA, F. C., HAN, S., BOAM, A., ZHANG, S., LIVINGSTON, A. G. Membrane aromatic recovery system (MARS): lab bench to industrial pilot scale. *Desalination*. 2002, **148**, 267–273.

[6] TANABE, H., OKOCHI, H., IGAWA, M. Separation of weak acids and bases by neutralization dialysis. *Ind. Eng. Chem. Res.* 1995, **34**, 2450–2454.

[7] ZHELEZNOV, A., WINDMÖLLER, D., KÖRNER, S., BÖDDEKER, K. W. Dialytic transport of carboxylic acids through an anion exchange membrane. *J. Membr. Sci.* 1998, **139**, 137–143.

[8] KOJIMA, T., NISHIJIMA, K., MATSUKATA, M. Removal and recovery of phenol from FCC effluent. *J. Membr. Sci.* 1995, **102**, 43–47.

[9] WANG, G., TANABE, H., IGAWA, M. Transport of glycine by neutralization dialysis. *J. Membr. Sci.* 1995, **106**, 207–211.

[10] DANCKWERTS, P. V. *Gas–Liquid Reactions.* New York: McGraw-Hill, 1970. ISBN 007015287X.

[11] GLASSCOCK, D. A., ROCHELLE, G. T. Numerical simulation of theories for gas absorption with chemical reaction. *AIChE J.* 1989, **35**, 1271–1281.

[12] LEVENSPIEL, O. *Chemical Reaction Engineering.* Third Edition. New York: Wiley, 1999. ISBN 0-471-25424-X.

[13] FROMENT, G. F., BISCHOFF, K. B., DE WILDE, J. *Chemical Reactor Analysis and Design.* Third Edition. Hoboken: Wiley, 2011. ISBN 978-0-470-56541-4.

[14] VAN KREVELEN, D. W., HOFTIJZER, P. J. Kinetics of gas–liquid reactions – Part I. General theory. *Rec. Trav. Chim.* 1948, **67**, 563–586.

[15] HIKITA, H., ASAI, S. Gas absorption with (m, n)-th order irreversible chemical reaction. *Int. J. Chem. Eng.* 1964, **4**, 332–340.

[16] PORTER, K. E. The effect of contact-time distribution on gas absorption with chemical reaction. *Trans. Inst. Chem. Eng.* 1966, **44**, T25–T36.

[17] YERAMIAN, A. A., GOTTIFREDI, J. C., RONCO, J. J. Mass transfer with homogeneous second order irreversible reaction. A note on an explicit expression for the reaction factor. *Chem. Eng. Sci.* 1970, **25**, 1622–1625.

[18] DE SANTIAGO, M., FARINA, I. H. Mass transfer with second order reaction. Numerical solution. *Chem. Eng. Sci.* 1970, **25**, 744–747.

[19] KISHINEVSKII, M. K., KORMENKO, T. S., POPA, T. M. Kinetics of gas absorption. *Theor. Found. Chem. Eng.* 1971, **4**, 641.

[20] DECOURSEY, W. J. Absorption with chemical reaction: development of a new relation for the Danckwerts model. *Chem. Eng. Sci.* 1974, **29**, 1867–1872.

[21] BALDI, G., SICARDI, S. A model for mass transfer with and without chemical reaction in packed towers. *Chem. Eng. Sci.* 1975, **30**, 617–624.

[22] WELLEK, R. M., BRUNSON, R. J., LAW, F. H. Enhancement factors for gas-absorption with second-order irreversible chemical reaction. *Can. J. Chem. Eng.* 1978, **56**, 181–186.

[23] KARLSSON, H. T., BJERLE, L. A general explicit enhancement factor for irreversible gas-liquid reactions with gas-side resistance. *Chem. Eng. Sci.* 1980, **35**, 1005–1007.

[24] LAST, W., STICHLMAIR, J. Determination of mass transfer parameters by means of chemical absorption. *Chem. Eng. Technol.* 2002, **25**, 385–391.

[25] WIJMANS, J. G., BAKER, R. W. The solution-diffusion model: a review. *J. Membr. Sci.* 1995, **107**, 1–21.

[26] NAGY, E. *Basic Equations of Mass Transport Through a Membrane Layer.* Second Edition. Amsterdam: Elsevier, 2019. ISBN 978-0-12-813722-2.

[27] ŠTĚPÁNEK, V., PALATÝ, Z., BENDOVÁ, H. Numerical analysis of dialysis with chemical reaction at steady state. Irreversible second-order reaction. *Chem. Eng. Process. Process Intensif.* 2015, **95**, 362–371.

[28] PALATÝ, Z., ŽÁKOVÁ, A. Modelling the flow of liquid in continuous dialyzer. *J. Membr. Sci.* 1998, **139**, 67–74.

[29] MICHAELS, A. S. Operating parameters and performance criteria for hemodialyzers and other membrane-separation devices. *Trans. Am. Soc. Artif. Intern. Organs.* 1966, **12**, 387–392.

[30] PALATÝ, Z., BENDOVÁ, H. Modeling and numerical analysis of counter-current dialyzer at steady state. *Chem. Eng. Process. Process Intensif.* 2010, **49**, 29–34.

List of student's published works

ŠTĚPÁNEK, V., PALATÝ, Z., BENDOVÁ, H. Numerical analysis of dialysis with chemical reaction at steady state. Irreversible second-order reaction. *Chem. Eng. Process. Process Intensif.* 2015, **95**, 362–371.

ŠTĚPÁNEK, V., PALATÝ, Z., BENDOVÁ, H. A critical comparison of approximate solutions for enhancement factor for irreversible second-order reaction. *Chem. Eng. Sci.* 2018, **191**, 410–419.

ŠTĚPÁNEK, V., PALATÝ, Z., BENDOVÁ, H. Modeling and numerical analysis of counter-current dialyzer with chemical reaction in stripping solution. *Chem. Eng. Sci.* 2020, **221**, 115641.