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Mass transport in biocatalytic membrane reactors

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Membrane bioreactor (MBR) technology is advancing rapidly around the world both in research and commercial applications (Strathmann et al., 2006; Yang et al., 2006). Integrating the properties of membranes with biological catalyst such as cells or enzymes forms the basis of an important new technology called membrane bioreactor. The MBR have been introduced several years ago and until now it is recommended for production of different, fine chemicals etc. (Yang et al., 2006; Belfort, 1989). The experiments are focused primarily on the hollow-fiber bioreactor with biocatalyst, either live cells or enzymes, inoculated into the shell and immobilized within the membrane matrix or in a thin layer at the membrane matrix-shell interface (Kelsey et al., 1990). Cells are either grown in the extracapillary space with medium flow through the fibers and supplied with oxygen and nutrients, or grown within the fibers with medium flow outside or across the fibers while wastes and desired products are removed. The main advantages of the hollow-fiber bioreactor are the large specific surface area (internal and external surface of the membrane) for cell adhesion or enzyme immobilization; the ability to grow cells to high density; the possibility for simultaneous reaction and separation; relatively short diffusion path in the membrane layer; the presence of convective velocity through the membrane if it is necessary in order to avoid the nutrient limitation (Piret and Cooney, 1991; Sardonini and DiBiasio, 1992).
The performance of a hollow-fiber or sheet bioreactor is primarily determined by the momentum and mass transport rate (Godongwana et al., 2007; Calabro et al., 2002) of the key nutrients through the bio-catalytic membrane layer. Thus, the operating conditions (trans-membrane pressure, feed velocity), the physical properties of membrane (porosity, wall thickness, lumen radius, matrix structure, etc.) can considerably influence the performance of a bioreactor, the effectiveness of the reaction. The main aim of this study is to give the mass transfer rates in presence of biochemical reaction in order to predict the concentration distribution and the effect of the reaction, through plane, biocatalytic membrane layer with constant or varied transport parameters. In this proceeding, mass transport accompanied by first-order reaction kinetics will be solved and discussed.

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1. Theory

The principle of the mass transport of substrates/nutrients into the immobilized enzyme/cells, through a solid, porous layer (membrane, biofilm) or through a gel layer of enzyme/cells is the same. Several investigators modeled the mass transport through this biocatalyst layer, through enzyme membrane layer or cell culture membrane layer (Brotherton and Chau., 1990; Piret and Cooney, 1991; Ferreira et al., 2001). Recently Nagy (2008) studied the mass transfer rate into a biocatalytic membrane layer with constant mass transport parameters. He defined the mass transfer rates for both side of the membrane surface. The rate equations are expressed as product of the mass transfer coefficient and driving force as it is traditionally applied for the diffusion systems, e.g. in gas-liquid systems. Main assumptions, made for expression of the differential mass balance equation to the biocatalytic membrane layer, are:

- Reaction occurs at every position within the biocatalyst layer;
- Mass transport through the biocatalyst layer occurs by diffusion and convection;
- The partitioning of the components (substrate, product) is negligible (Thus, $C^*=C^*_m$; see Fig. 1);
- The effect of the concentration boundary layer should also be taken into account;

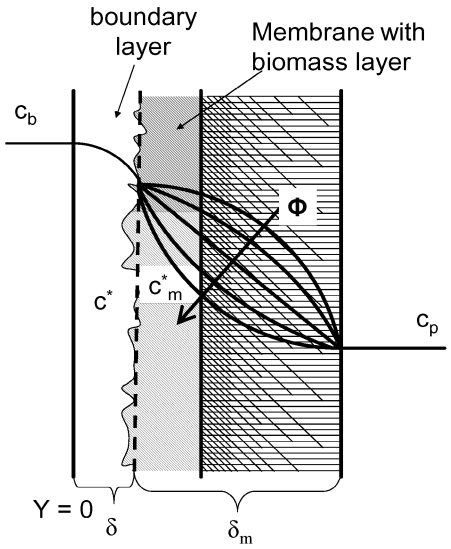

Fig. 1. *The membrane layer with biomass with thickness of δ_m and the concentration polarization layer with thickness of δ. C^* and C_m^* are concentrations on the liquid-membrane interface (→: increasing reaction modulus)*

The membrane layer with biomass colony on it and the concentration boundary layer are illustrated, with important notations and concentration profiles, in *Fig. 1*. The membrane concentration, C is given here in a unit of measure of gmol/m^3. This can be easily obtained by means of the usually applied in the e.g. g/g unit of measure with the equation of $C=w\rho/M$, where w concentration in kg/kg, ρ – membrane density, kg/m^3,

M-molar weight, kg/mol. In this proceeding the mass transport will be showed for the case with constant parameters as well as for first-order reaction. For the sake of simplification, let us regard a steady-state reaction as well as let us use the Cartesian co-ordinate

1.1 Mass transfer accompanied by first-order reaction

First let us look at the equation for the membrane reactor, only. Thus the effect of the concentration boundary layer is neglected, thus $C_b=C^*$. The differential mass balance equation in the case of constant transport parameters is as follows:

$$D_m \frac{d^2C}{dy^2} - \upsilon \frac{dC}{dy} - k_1 C = 0 \tag{1}$$

Let us look at the biocatalytic membrane layer without concentration boundary layer. Thus, the boundary conditions are as (the mass transfer resistance in the boundary layer is neglected here, thus $C^*=C_b$ and the place y=0 means here the inlet interface of the membrane layer):

at y=0 $C=C_b$ (2)

at $y=\delta_m$ $C=C_p$ (3)

The general solution of Eq. (1), applying standard methodology (for details of solution (see Nagy, 2008) will be as follows ($Y=y/\delta_m$):

$$C = T_m e^{\lambda Y} + P_m e^{\tilde{\lambda} Y} \tag{4}$$

The "overall" mass transfer rate, namely the sum of the diffusive and the convective mass flow, can be expressed as:

$$J = -D_m \left.\frac{dC}{dY}\right|_{Y=0} + \upsilon C|_{Y=0} \equiv k_m^o \left(\tilde{\lambda} T_m + \lambda P_m\right) \tag{5}$$

According to Eqs. (4) and (5), the J value can be expressed as follows:

$$J = \beta\left(C_b - K C_p\right) \tag{6}$$

$$\beta = k_m^o \frac{\left(Pe_m/2\right)\tanh\Theta_m + \Theta_m}{\tanh\Theta_m} \tag{7}$$

$$K = \frac{\Theta_m e^{-Pe_m/2}}{\cosh\Theta_m \left\langle \left(Pe_m/2\right)\tanh\Theta_m + \Theta_m \right\rangle} \tag{8}$$

and

$$\lambda = \frac{Pe_m}{2} + \Theta; \qquad \tilde{\lambda} = \frac{Pe_m}{2} - \Theta; \qquad \Theta = \frac{Pe_m}{2}\sqrt{1+2\xi^2}$$

$$Pe_m = \frac{\upsilon \delta_m}{D_m}; \qquad \Phi = \sqrt{\frac{k_1 \delta_m^2}{D_m}}; \qquad \xi = \sqrt{\frac{k_1 \delta_m}{\upsilon}}; \qquad k_m^o = \frac{D_m}{\delta_m};$$

The Φ defined here is the well known Thiele modulus defined for the catalyst membrane layer while the Peclet number corresponds to the often used Bodenstein number. The ξ dimensionless variable is the ratio of the reaction rate and the convective flow.
Similarly to Eqs. (4) and (6), the concentration distribution and the mass transfer rate at membrane interface, without chemical reaction can be given (see Nagy, 2008).

1.2 The two-layer (boundary- and membrane layer) mass transfer rate
The value of the two-layer mass transfer rate, J, can be given, as follows (Nagy, 2008):

$$J = \beta_{tot}\left(C_b - Ke^{-Pe_L} C_p\right) \tag{9}$$

where

$$\beta_{tot} = \frac{1}{\frac{1}{\beta_L^o} + \frac{e^{-Pe_L}}{\beta}} \tag{10}$$

with

$$\beta_L^o = k_L^o Pe_L \frac{e^{Pe_L}}{e^{Pe_L} - 1} \equiv \frac{D_L}{\delta_L} \frac{Pe_L}{2} \frac{e^{Pe_L/2}}{\sinh(Pe_L/2)}; \quad k_L^o = \frac{D_L}{\delta_L}; \quad Pe_L = \frac{\upsilon \delta_L}{D_L}$$

The subscript L denotes here the boundary layer.
The mass transfer rate can be given for zero-order reaction, similarly. For its details see Nagy's paper (Nagy, 2008)

2. Results

The axial and radial depletion of substrate, e.g. oxygen, nutrient, can be often critical scale-limiting factor in cell culture hollow fiber reactor (Ferreira et al., 2001). In order to increase of the substrate concentration in the membrane bioreactor, sufficient diffusion rate and/or convective flow has to be provided through the lumen, in axial direction, and through the membrane layer, in radial direction, of a hollow fiber. Typical operating conditions of a hollow fiber bioreactor were applied (*Table 1*) to calculate the inlet and outlet mass transfer rates of a substrate. From that, the effectiveness of the bio-catalytic reaction as well as sufficiency of the nutrient supply could be estimated.

Table 1. Membrane module characteristics and physical parameters applied for calculation of the mass transfer rates into and out of a sheet membrane (Brotherton and Chau , 1990; Piret and Cooney, 1991)

Pe-number:	0.1-10
Thiele-modulus, Φ:	0.1-5
Diffusion coefficient:	10^{-9}-10^{-10} m^2/s
Membrane thickness:	(100-1000) x10^{-6} m

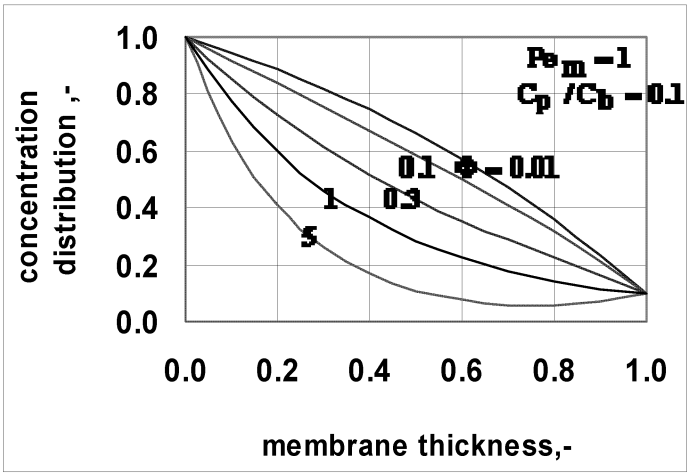

Fig. 2 *The concentration profiles of mass transport through a biocatalytic membrane layer accompanied by first-order biochemical reaction.*

The effect of the convective velocity on the concentration profiles is illustrated in *Fig. 2*. The relative value of the outlet concentration was chosen to be 0.1. This value is assumed to be needed by microorganisms to grow without damage. Thus, the substrate concentration should be maintained above the given critical level throughout the biocatalytic membrane layer. Decreasing Pe_m values, the concentration profile, in limiting case, namely $Pe_m \rightarrow 0$, tends to be linear indicating that the transport occurs by diffusion, only. With the increase of the Pe_m value, the concave curvature of the curves increases rapidly. Let us look typical examples for the enhancement as a function of the biochemical reaction rate. Regarding single layer mass transfer (mass flow without mass transfer resistance in the boundary layer), the enhancement increases without limit as a function of the reaction rate (*Fig. 3*). This behavior is similar to that of gas-liquid diffusive mass transfer. According to parameters Φ and Θ [Eq. (8)], the value of Pe_m and reaction rate constant, Φ, can be varied, independently. With the increase of the Peclet number, the effect of the reaction rate strongly lowers. It is to note that the boundary layer mass transfer resistance is not taken into account by the above figures. It can strongly influence both the concentration distribution and the enhancement. It is easy to estimate its effect by means of Eq. (9).

3. Conclusion

It has been proved that the simultaneous diffusive and convective mass transfer rate can also be expressed as product of a mass transfer coefficient and the driving force, similarly to that of the diffusive mass transfer coefficient given for gas-liquid or liquid-liquid systems.

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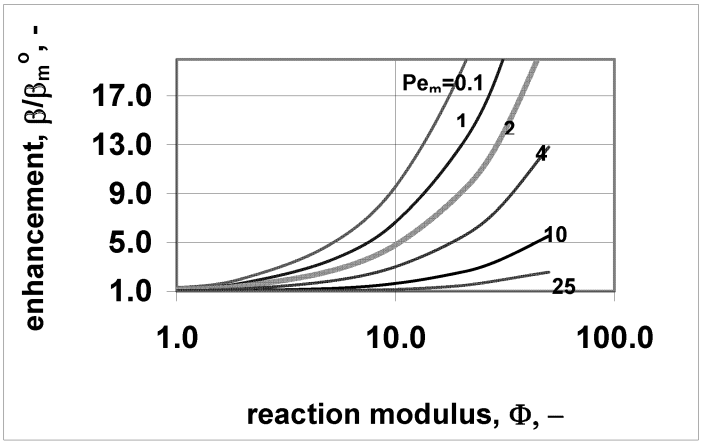

Fig. 3 Enhancement of the inlet mass transfer coefficient for the biocatalytic membrane layer without concentration boundary layer. (C_p/C_b=0.1)

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