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Description of the diffusive–convective mass transport in a hollow-fiber biphasic biocatalytic membrane reactor

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ABSTRACT

The substrate transport in a biphasic, biocatalytic, capillary membrane layer has been investigated. The measured data of oleuropein hydrolysis, in olive mill wastewater, have been evaluated in both a well-mixed tank reactor and a polysulphone, biocatalytic, capillary membrane reactor. The β-glucosidase enzyme was immobilized in the sponge layer of the asymmetric, hydrophilic membrane layer. Strong, competitive product inhibition, applying Michaelis–Menten kinetics with product inhibition for evaluation of the measured data, has been obtained in the mixed tank reactor while the reaction did not show inhibition in the biocatalytic membrane layer. Applying the kinetic data for the oleuropein hydrolysis, the performance of a biocatalytic membrane reactor has been discussed under different operating modes. The effect of the lumen radius, membrane thickness, location of the inlet of the substrate, the inlet concentration and Peclet number as well as the effect of the external mass transfer resistances have been discussed and illustrated. It has been shown that all parameters mentioned above can have a strong effect on membrane performance. The model and its presented, so-called forward sweep numerical solution method, where concentration of the first sublayer is given by an explicit expression of closed form, can essentially help the reader estimate the effect of the operating parameters on the performance of a biocatalytic, capillary membrane reactor. The simulation results enable the user to select the right choice between operating conditions, providing a high efficiency membrane reactor.

1. Introduction

Enzymatic bioconversion processes are of increasing use in the production, transformation and valorization of raw materials [1]. Their important applications have been developed in the field of food industries, manufacture of fine chemicals, particularly pharmaceuticals or application for environmental purposes, e.g. decomposition of toxic chemicals and organic dyes [2,3]. Membranes, especially the asymmetric ones, are thought to be good supports for immobilization of enzymes by physical or chemical interaction in or on the membrane, where enzymes can be covalently or non-covalently linked to internal and/or external interfaces of the membrane or entrapped in the membrane [4–6]. The enzyme is more often immobilized in the sponge layer [7–10] of the membrane (covalently linked, entrapped, non-covalently linked) or on the skin modified (grafting, etching, coating) membrane surface [4,11]. Various membrane materials, hydrophobic, hydrophilic or organic and inorganic, can be used as bioreactor while the membrane layer can be used either in flat sheet or in fibrous form. Depending on the solubility of the substrate(s) and reaction product(s), the bioreactor can be monophasic or biphasic regarding the flowing fluid phases. As monophasic reaction can be mentioned the oxidation/reduction reactions using, e.g., peroxidase, glucose oxidase, laccase [4,12], or removal of toxic chemicals from the environment taking place in aqueous phase [13–15]. In this case, the substrate is often forced to flow through the biocatalytic membrane; thus one of the interesting advantage of this operating mode is the diffusion flow along with mostly the more intensive convection flow makes the reaction more effective [4]. When the substrate is a hydrophobic compound, the biphasic system is often applied for the bioreaction, especially when the product is soluble in aqueous phase. Lipase enzymes are mostly used in organic synthesis as hydrolysis [7,9,16–18] and esterification [7,19,20], or kinetic resolution of racemates for production of optically pure isomers [7,10,11,21,22]. The organic and aqueous phases are separately recirculated on the lumen and shell sides of the membrane, following the criteria that the phase containing the substrate should always be recirculated along the side of the membrane containing the immobilized enzyme [7].

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An appropriate mathematical model is indispensable in order to be able to estimate the effect of the reaction parameters, as enzyme concentration, reaction kinetic constant, conversion, and the effectiveness of the reaction. The Michaelis–Menten kinetics is used in most cases, but this kinetic model does not involve the diffusive and convective transport of the reactant inside of the membrane. If there is diffusion limitation then the differential mass balance equation should take into account the effect of the bioreaction on the mass transport. Applying capillary or plane biocatalytic membrane, three regions can be distinguished, namely the two sides of the membrane (the lumen and the shell sides) and the membrane itself [23–26]. Several authors analyzed the diffusive–convective mass transport in the lumen, and shell as well as in the membrane matrix [23–25]. These studies have predicted the concentration distribution in every layer in the case of single-phase mass transport, only. Our paper focuses on the mass transport through a capillary biocatalytic membrane layer in two-phase systems, namely when the substrate cannot enter the second immiscible phase. As it will be shown, the difference between these operating modes is caused by the different boundary conditions at the outlet side of the membrane reactor. The fluid phases are often recirculated; thus, their concentration change in a capillary module is not generally important. Otherwise, the mass transfer rates defined for both sides of the membrane should be replaced in the mass balance equation of the fluid phases. The biocatalyst (enzyme) is mostly immobilized (either physical adsorption methods or by chemical linkage [27]) into the internal interface of the porous sponge layer or onto the dense membrane interface in a hydrogel layer [28–30]. The complete description of the catalytic membrane layer needs the solution of the complex Navier–Stokes flow models applying the component mass balance and/or momentum balance equations [23–26,31–34]. The momentum balance equation can often be neglected; thus suitable mass balance equations are often used and recommended for the biocatalytic membrane layer [10,11,23,25,33,34]. The diffusion plus biochemical reaction model is the most often applied mass transport description independently that the biocatalyst is immobilized onto the membrane surface in a hydrogel layer [16,30] or in the internal interface of the porous support layer [7–9,22,33]. This mass balance equation has mostly been solved numerically applying the general Michaelis–Menten kinetics. Often the reactant phase is forced to pass through the membrane pores, inducing additionally convective flow through the membrane [10,11,15,32,34]; accordingly the mass balance equation should be extended by a convective term, as well. Recently Nagy [26] and Nagy et al. [35] analyzed the diffusive–convective mass transport in enzyme membrane bioreactors applying ultrafiltration (i.e. without sweep phase) and recirculation modes (i.e. with sweep phase). They defined the mass transfer rate through the biocatalytic membrane in closed mathematical forms, in limiting cases of the Michaelis–Menten kinetics, in the presence of diffusive and convective flows.

A detailed analysis of diffusion–convection mass transport through a biocatalytic, capillary membrane, applying biphasic systems, is missing in the literature, which analyzes the mass transfer properties, namely mass transfer rates, concentration distribution depending on the cylindrical effect of a hollow fiber membrane and effect of the reaction rate as well as operating modes and location of the inlet fluid phase. The diffusion–convection mass transport process, with zero concentration gradient on the outlet side of a capillary membrane bioreactor, is a hardly known process. On the other hand, the effect of the polarization layer is mostly neglected during the calculations. In the diffusive–convective mass transfer rate, the concentration distribution will be analyzed in a cylindrical membrane bioreactor in the presence of a reaction with substrate hindered Michaelis–Menten kinetics. Additionally, the role of the fluid boundary (other saying polarization) layer will also briefly be discussed. A forward numerical solution methodology was developed, the usage of which is much easier than that of the often-recommended Thomas method. According to the solution developed, the mass transfer rate is expressed in a single, closed, explicit mathematical form. All results presented will be shown through an example of the production of isomer of oleuropein aglycon from oleupropein by means of immobilized β-glucosidase in the sponge layer of polysulphone capillary membrane [36–38]. This solution can be recommended for evaluation of biocatalytic processes in the membrane reactor adapting it to the operating modes.

2. Theory

A simplified physical model and the mathematical model of biocatalytic reactors will shortly be discussed with membrane as supporters (catalyst is immobilized on its skin surface) or is an asymmetric biocatalytic membrane layer where the catalyst (enzyme) is immobilized in the sponge matrix.

2.1. Physical models of these systems

The biocatalyst can be immobilized onto the skin-layer surface of the membrane as a hydrogel or into the porous sponge layer, onto its internal surface. In this latter case the membrane is used as a carrier or matrix for immobilization as well as a selective barrier. Substrate molecule should reach and come into contact with the immobilized enzyme molecule and this substrate transport can be governed by the hydrogel or the polymeric membrane properties depending on the immobilization mode. One of the important advantages of the membrane bioreactor is that the diffusive flow can be combined by transverse flow (convective flow through the membrane matrix) and thus the transport can be more intense than that in the case of diffusive flow, only [4,26,35,39]. A simplified physical model of these systems is illustrated in Fig. 1. Let us look briefly at the important operating modes of these two immobilization cases. A single biocatalytic reaction occurs in the hydrogel layer or in the sponge matrix [A+B↔C+D]. Often one of the reactant and products is hydrophilic while the other one is hydrophobic.

2.1.1. Enzyme is immobilized into its porous sponge layer (Fig. 1A)

The biocatalyst is immobilized into the internal surface of the mostly modified membranes, to make them suitable for immobilization. Three categories are distinguished in Fig. 1A, namely i) the two phases are in contact on the external interface of the sponge layer (A_1); ii) due to the higher pressure on the shell side, the substrate-containing phase (aqueous or organic) partly enters the porous layer with a given penetration depth (A_2) as well as iii) the substrate-containing phase is pressed by given transmembrane pressure through the biocatalyst membrane (A_3) inducing given value of convective flow. The biochemical reaction takes place at the interface of the phases where enzyme is also present, in the biphasic system. The aqueous microenvironment (water molecules form an aqueous layer near the active site of the enzyme) of immobilized enzyme should provide the necessary ternary or quaternary enzyme structure for biocatalytic reaction. The reactant(s) (e.g. hydrolysis, epoxidation, peroxidation, esterification, transesterification, etc. reactions have reactants in both phases) should be transported from the bulk phase(s) to the interface between the phases where the biocatalytic reaction mainly takes place. Note that the reaction can partly take place in the aqueous phase when the organic reactant can dissolve in this phase. As Fig. 1 illustrates the reactant should diffuse from the bulk shell phase through the pores to reach the biocatalyst and the reaction partner, (if there is it at all) in the other (organic or aqueous) phase. When this phase is moving from the shell side through the biocatalytic membrane into the lumen fluid phase as drops then the convective velocity should also be involved in the mass