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Modeling of a biphasic membrane reactor catalyzed by lipase immobilized in a hydrophilic/hydrophobic composite membrane

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Abstract

A diffusion-reaction model suitable for high enzyme loading density was developed to describe the situation of immobilized lipase in the hydrophilic cellulose acetate (CA)/hydrophobic polytetrafluoroethylene (PTFE) composite membrane. Under this situation, not all the immobilized enzyme was found to be effective, and as such, a utilization coefficient of immobilized lipase was proposed. In this paper, two different reaction systems (racemic ibuprofen ester chiral separation and olive oil hydrolysis) using immobilized lipase in hydrophilic/hydrophobic composite membrane was studied. The former system is reaction controlled and the latter is diffusion controlled. The utilization coefficient of lipase catalyzing the racemic ibuprofen ester was from 83% to 39%, decreasing with the increasing of enzyme loading from 0.3 to 2.1 g m^{-2}. The calculation values were found to be consistent with the experimental data through the utilization coefficient of lipase, which was obtained by the first system to predict the reaction rate of the second one. The effect of substrate concentration and membrane structure on the activity of the immobilized lipase was investigated with this model. We conclude that (1) the effect of substrate concentration is double-edged, (2) utilization coefficient of lipase decreases with the increasing of enzyme loading, (3) composite membranes with thinner and more porosity hydrophobic layer leads to higher reaction rate.

Keywords: Reaction-diffusion model; Composite membrane; Lipase immobilization; Hydrolysis

1. Introduction

Lipase (EC 3.1.1.3 L1754) is widely used in biochemical and fine chemical industries as a catalyst for hydrolysis and esterification. It has been proven that due to its special structural characteristics [1], lipase can catalyze both organic and aqueous substrates in the organic/aqueous interface where it shows much higher activity [2]. Although diffusion resistance was introduced, immobilization in solid support can enhance the usefulness of the lipase overall [3] in the way of improving its stability, activity and reusability. Meanwhile, membrane is widely used as support for lipase immobilization. Biphasic membrane reactors are used in large varieties of chemical industry due to its other advantages as well as its ability to integrate the reaction and separation process in one unit [4].

The mathematical model of catalytic biphasic membrane reactor was employed by many researchers. In his study, Long et al. had set up a model of enzymatic hollow fiber membrane reactor, where the process were divided into diffusion in the fiber lumen and reaction in the membrane matrix, after which nonliner partial differential equations was used to describe the process in the membrane [5]. Trusek-Holownia had set up a model to describe a two-liquid phase system catalyzed by a catalytic membrane, where the lipase was assumed to form a gel layer in the membrane matrix [6]. Curcio et al. used unsteady-state momentum and mass balance equations to describe a membrane reactor with immobilized enzyme, with the modeling result showing high agreement with the experimental data [7]. However, most of these studies ignored the relationship between the enzyme utilization coefficient and the amount of enzyme loading, such that they were able to obtain an accurate measurement at the low enzyme loading situation but fail to accurately measure the decline when the enzyme loading goes up. In this study, the factor of enzyme loading to enzyme utilization coefficient was considered, and the resulting model was able to accurately describe the situation when the enzyme loading was high.

In our previous work [8–10], a hydrophilic/hydrophobic composite membrane with special micro structure was introduced as

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the support of lipase. The composite membrane was composed of two parts: the hydrophilic part of CA and the hydrophobic part of PTFE, whose layers are relatively dense and porous, respectively. During the ultrafiltration process, most lipase molecules were trapped in the interface of the CA and PTFE layers. As a result, when the amount of trapped lipase molecules goes up, most of them packed together and may form a gel layer. The lipase loading is up to 2.1 g m^{-1} in this work, higher than many of the other researchers. An enzymatic biphasic membrane reactor using this kind of composite membrane was introduced. There lipase was immobilized in the microstructure of the composite membrane. The experiments were done under 40 °C except specially mentioned, atmospheric pressure, and two reaction systems of the hydrolysis of olive oil and the chiral separation of racemic ibuprofen ester were studied.

2. Theory

2.1. The reaction-diffusion model

Fig. 1 shows the schematic of the reaction-diffusion model of the hydrolysis of substrate (olive oil or (*S*)-ibuprofen ester) in a biphasic membrane reactor. The reaction was catalyzed by the lipase immobilized in the composite membrane. As can be seen, the hydrophobic layer, which is a catalytic layer, is divided into a diffusion zone and a reaction zone. Almost all of the lipase molecules are packed at the interface of the hydrophilic/hydrophobic layers, in the hydrophobic layer which formed an enzymatic gel layer that is known as the reaction zone. While in diffusion zone there is few lipase molecule. The substrate in the organic phase diffuses through the diffusion zone without reaction, while in the reaction zone, the substrate is hydrolyzed by immobilized lipase while diffusing. Meanwhile, the hydrophilic layer retains enzymes and insulates the immobilized lipase from the flow of the aqueous phase. The effect of the hydrophilic layer on the diffusion and reaction of the substrate is thus to be slight and negligible. As this model can serve both two systems, only one common set of symbols were employed.

2.1.1. The diffusion zone

In the diffusion zone, the mass transfer of the substrate is considered a one-dimensional steady-state diffusion without the reaction. The diffusion equation is:

$$J_0 = D_m \frac{dc}{dx} \tag{1}$$

or after integration

$$c = c_0 - \frac{J_0}{D_m} x \tag{2}$$

where J_0 is the substrate flux in the interface between the hydrophobic layer and the organic phase, c_0 and c are the substrate concentration in the interface between the hydrophobic layer and the organic phase and inside the layer, respectively, D_m is the diffusion coefficient of the substrate in the diffusion zone, and x is the coordinate location in the CA layer. Using Eq. (1) and conservation equation, with proper boundary conditions, the substrate concentration in any location in the diffusion zone can be calculated.

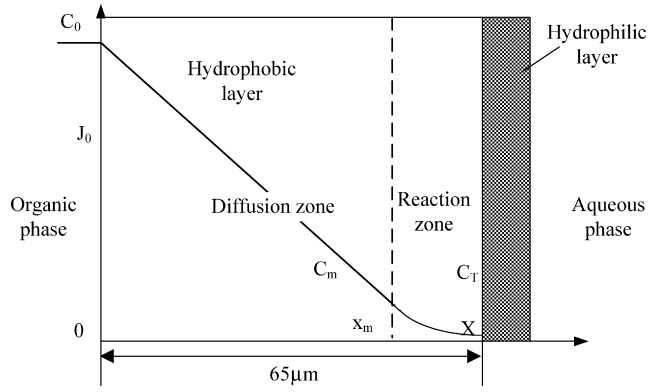

Fig. 1. Reaction-diffusion model.

2.1.2. The reaction zone

In the reaction zone, the substrate is hydrolyzed by immobilized lipase while diffusing. The mass balance equation is

$$-R_c = D'_m \frac{d^2c}{dx^2} \tag{3}$$

where R_c is the reaction rate and D'_m is the diffusion coefficient of the substrate in the reaction zone.

The following boundary conditions are obtained:

At x_m, where is the interface between diffusion and reaction zone, the substrate concentration equals

$$c_m = c_0 - \frac{J_0}{D'_m} x_m \tag{4}$$

And the substrate concentration gradient equals:

$$\left.\frac{dc}{dx}\right|_{c_m} = -\frac{J_0}{D'_m} \tag{5}$$

At X the position of the interface of the hydrophilic/hydrophobic layer, the substrate cannot leave the layer because it does not dissolve in the aqueous phase, and for this reason the substrate concentration gradient is zero:

$$\left.\frac{dc}{dx}\right|_{X} = 0 \tag{6}$$

Eqs. (5) and (6) yielded the values for c_m and $dc/dx|_{c_m}$, while Eq. (3) is calculated stepwise from x_m toward X. The calculation is then repeated with different J_0 until the boundary condition of Eq. (6) is reached. As the activity of enzyme is losing during the reaction, the reaction rate is decreasing, in our work the initial reaction rate (the rate when the reaction was just started) R_0 is studied. R_0 could be calculated with the following equation:

$$R_0 = J_0 S_m \tag{7}$$

where S_m is the membrane area.