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Modelling diffusivity in porous polymeric membranes with an intermediate layer containing microbial cells

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Abstract

Three-layer systems (membrane – composite layer (cells + polymer) – membrane) are important in different biochemical applications. Models of latex layered-membranes were evaluated and compared with experimental data in order to predict the diffusivity of substrates in the composite layer containing living *E.coli* microbial cells. Diffusivity predictions are dependent on the presence or the absence of a 'skin' layer, on the degree of polymer particle coalescence and on the thickness of each layer. Simulations with layered models were made to identify the dominant mechanisms in the three-layer system. It was found that the layered system is sensitive to the latex coatings porosity when the composite layer occupies less than 50% of the total membrane system thickness. Whenever the control of polymer particle coalescence and of the layers (coating/composite layer) thickness may be achieved, multi-layer systems presenting a wide range of relative diffusion conductivities may be built for different types of living cells and for a wide variety of practical applications. The diffusivity of the latex layer is proportional to the square of latex porosity.

Keywords: Diffusion; Microporous membrane; Immobilised cells; Modelling; Packing; Mass transfer

1. Introduction

Multi-layer microporous systems have a wide application in industry and biotechnology and their general models are described in numerous publications [1–9]. In the biotechnology layered systems have a broad application [10] including, in particular, systems containing living cells: thick-film and immobilized cell biosensors [11–14], components of bioelectronic devices [15–17], or biocatalytic coatings [18].

Among these systems we may distinguish porous layers and membranes, which are forming by polymer latex of sub-micron sizes [19,20]. Concerning the biocatalyst application, such systems have a structural diversity of membranes and composite (cell + latex) layers because of particle size distribution, shape, layers thickness, packing and formation conditions as well as technological demands [18,21–23]. The promising type of thin-membrane bioreactor consists of a high volume fraction of viable, metabolically active whole cells imprisoned in a porous polymeric matrix of partially coalesced latex particles that are substantially smaller than the bacterial cells.

A method for immobilising viable but non-growing *Escherichia coli* in highly uniform patches was considered by Lyngberg et al. [21]. The method allows the composite (cell + polymer) layer and the polymer sealant to be variable in thickness from 5 to 60 μm and from 7 to 80 μm, respectively.

The polymer latex coating micro-structure for whole-cell biocatalyst application was investigated by microscopy [22]. Results showed that porosity and permeability can be controlled by appropriate drying and rehydration protocols. Evidence shows that glycerol retards particle deformation, compaction, and coalescence. The microstructure of a biocatalytic latex coating containing viable *E. coli* cells was analysed in [23,24]. The cells are physically entrapped by the latex particles and not chemically bound to them and cells were uniformly distributed in the matrix.

Another multi-layer system, a permeable biocatalytic coating of thin layers of 280 nm particle size latex containing *E. coli* mixed with latex particles, was also investigated in the work of Lyngberg et al. [18]. The effective diffusion coefficient D_e of the system was measured and compared with those D_0 in bulk

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Nomenclature

D_0	diffusion coefficient in bulk liquid (m^2/s)
D_e	effective diffusion coefficient (m^2/s)
h	diameter of the rod (m)
K	overall mass transfer coefficient (m/s)
k	mass transfer coefficient of the multi-layer system (m/s)
k_{p1}, k_{p2}	respectively, mass transfer coefficients in phase 1 and 2 separated by the layered system (m/s)
k_i	mass transfer coefficient in i-th layer (m/s)
L	multi-layer system thickness (m)
L'	diffusion pathway (m)
l_i	thickness of i-th layer (m)
m	number of sub-layers in the composite layer
n	number of layers in the system
T	tortuosity
x_c	volume fraction of cells in the composite layer
y_i	linear fraction of i-th layer thickness in the total system thickness
ε_c^0	porosity of pure cell packing
ε_i	the i-th layer porosity
ε_{lx}^0	porosity of pure latex packing
δ	ratio of the cell length/diameter
ϕ_c	cell volume concentration in the composite layer
$\eta = D_e/D_0$	system relative diffusion conductivity
τ	tortuosity factor
τ_i	tortuosity factor of i-th layer

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c	cell fraction
clx	composite layer (cells + latex)
i	characteristics of i-th layer
j	characteristics of j-th sub-layer in the composite layer
f	polymer film characteristics
lx	latex layer in the form of the spherical particles packing
lx + s	latex layer with skin
lx + clx + s	three-layer system with skin on the border of one of the latex coating
s	skin (layer) of the flattened latex particles
sp	skin with distributed within pore space dispersed phase or polymer film

fluid. It was found that a ratio $\eta = D_{lx}/D_0$ of latex coatings varies from 3×10^{-4} for unmodified latex coating to 6.8×10^{-2} for coatings containing sucrose, where D_{lx} is the effective diffusion coefficient in the latex layer. The results were explained by postulating a flattening of the latex particles against the surface of the solid substrate on which the coating was cast, as well as by the presence of a colloid stabiliser. Latex coatings were cast on stainless steel and delaminated to build three-layer composites containing viable *E. coli* mixed with latex particles in the middle layer.

The term diffusivity is generally used with the same meaning as diffusion coefficient (see: "Chemical diffusion coefficient, Fick's first law, partial diffusion coefficient" [80]) and will be used in this work meaning a "capacity to allow diffusion" [81]. Several effects acting on the diffusivity of layered systems can be identified: micro-structure of the composite layer is dependent on the packing structure, on density as well as on a particle (cell/latex) size ratio, thickness, structural characteristics of the coatings, among others [18,22]. A detailed overview of the layered systems to be considered in this work may be found in recently published papers [78,79].

2. Theoretical background

A multi-layered system may be characterised by a conventional mass transfer model [2,6,25,26]. A layered permeable system mass transfer coefficient K, in general, depends on the phase conditions and on the layered system properties; if the system is in-between phases, then $1/K = 1/k_{p1} + 1/k + 1/k_{p2}$, where k_{p1}, k_{p2} and k is, respectively, the mass transfer coefficients in phase 1, 2, and in the layered system. When the mass transfer resistance is concentrated at the permeable layers, then it is possible to assume that $1/K \cong 1/k$ and for diffusion through the layered system the above expression is simplified to

$$\frac{1}{k} = \sum_{i=1}^{n} \frac{1}{k_i} \tag{1}$$

where k is the n-th layer system mass transfer coefficient, k_i is the mass transfer coefficient of the i-th layer, and n is number of layers in the system.

If diffusion is not affected by a hindrance effect [27] and assuming also that, different layers have different porosity and tortuosity, then the mass transfer coefficient k_i is represented as

$$\frac{1}{k_i} = \frac{l_i \tau_i}{(D_0 \varepsilon_i)} \tag{2}$$

where D_0 is the diffusion coefficient of solute in bulk liquid and for the i-th layer, l_i is the layer thickness, τ_i is the tortuosity factor, and ε_i is the layer porosity.

The problem becomes more complex in the case of a non-homogeneous system with significant differences in porosity and tortuosity [26,28–32].

In the case of immobilised cells, depending on conditions, cells may be distributed non-homogeneously within the porous matrix. The non-homogeneous cell distribution may have the form of a confined cell sub-layer in a composite layer with an anisotropic cell concentration distribution [33,34]. Cells may be distributed, for instance, with a gradual concentration in the total volume of the porous medium. They may also be different in shape, spatial orientation, type of aggregation of the microbial population, etc. [35–44]. The immobilised cell system effective diffusivity is therefore, affected by two main components: polymer composition; cell presence and cellular spatial distribution [45,46].

In general, multi-layer systems may have either a capillary nature or a structure generated by monosize particle packing, by