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Surface reactors for photocatalytic water purification – a mass transfer evaluation

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ABSTRACT

This paper presents numerical experiments of mass transfer and kinetics influence on the overall effect in the case of surface reactors, which could be used in photocatalytic water purification. The examined model was based on an assumption that the reaction occurs on the plate surface and that the substrate is developed via vertical dispersion in gravitational laminar stream flow. The discussion is based on the calculation of degree of substrate conversion maps for different Damköhler and transverse Peclet numbers. The obtained results allow to estimate how operation parameters affect the overall reaction to mass transfer limitation.

Keywords: Mass transfer limitation; Surface reactor; Photocatalysis; Laminar flow; Water purification

1. Introduction

Surface reactors with gravitational laminar liquid flow may be used in photocatalytic processes [1]. Photocatalysis provides non-selective oxidation for even hazardous water poisons. Moreover, aqueous conditions are highly desirable here. In the case of heterogeneous photocatalysis, the limitation of mass transfer occurs; a strong influence even for slurry reactors with relatively small aggregates of photocatalyst [2] and in microchannel reactors for immobilized one [3] has been proved. The mass transfer limitation works focus generally on devices operating under the plug-flow regime [3,4]. Moreover, most of works are based on the first Damköhler number and only several works have been proposed using second Damköhler number [5]. There is no work which takes into account the diffusive mass transfer effect in photocatalytic reactor.

Using simple, sloped plate with immobilized catalyst not only provides a simple structure of the reactor but also provides other advantages: more light may penetrate the liquid (no turbulence) and the stream is still oxygenated because it is open up to the air.

On mathematical modeling, two dimensionless numbers were chosen to describe the operation regime: the transverse Peclet number and the second Damköhler number. The Damköhler number is defined by a comparison of the reaction ratio with the rate of mass transfer. Practically, if the second Damköhler number is above 10 or below 0.1, the degree of substrate conversion tends to the values above 0.9 and below 0.1, respectively [6]. Another advantage of using the second Damköhler number is that the analysis may be carried out for a variety of orders of process kinetics.

$$\mathrm{Da}_{\mathrm{II}} = \frac{kc_{A0}^{m-1}}{ak_{\mathrm{mass}}} \tag{1}$$

The transverse dispersion coefficient is commonly used in describing the transverse mass transfer in case of laminar liquid flow [7,8]. Here we applied the transverse Peclet number, which can be expressed by Eq. (2). It describes the intensity of transverse dispersion effect which is responsible for the intensification of mass transfer to the reacting surface.

$$\mathrm{Pe}_z = \frac{UH^2}{DL} \tag{2}$$

Damköhler and transverse Peclet numbers represent operational conditions of the surface laminar gravitational liquid flow reactor.

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Details of the operational mode of such a device may be optionally included in the mathematical model. The model of surface reactor gravitational laminar liquid flow is derived in the following sections.

2. Mathematical model

The scheme of the reactor contains its dimensions as presented in Fig. 1.

The mathematical model is based on mass balance of the substrate:

$$dhdls\frac{\partial c_A}{\partial t} = Usdh\left(c_A - c_A\frac{\partial c_A}{\partial l}dl\right) - Dsdl\left(\frac{\partial c_A}{\partial h} - \frac{\partial c_A}{\partial h} - \frac{\partial}{\partial h}\left(\frac{\partial c_A}{\partial h}\right)dh\right) \quad (3)$$

Since most of the works in photocatalysis suggest pseudo-first order reaction [2–5], in this paper we assumed that the order is equal to 1. Thus the reacting surface may be balanced by the following expression:

$$sdl\frac{\partial c_A}{\partial t} = -Dsdl\frac{\partial c_A}{\partial h} - sdlkc_A \quad (4)$$

In steady-state Eqs. (3) and (4), the following are presented:

$$\frac{\partial c_A}{\partial l} = \frac{D}{U}\frac{\partial^2 c_A}{\partial h^2} \quad (5)$$

$$\frac{\partial c_A}{\partial h} = \frac{-kc_A}{D} \quad (6)$$

Then the following dimensionless variables are introduced:

- degree of substrate conversion:

$$\alpha = \frac{c_{A0} - c_A}{c_{A0}} \quad (7)$$

- dimensionless length of the reactor:

$$x = \frac{l}{L} \quad (8)$$

- dimensionless height of a liquid film:

$$\xi = \frac{h}{H} \quad (9)$$

After that the model is expressed as:

$$\frac{\partial \alpha}{\partial x} = \frac{DL}{UH^2}\frac{\partial^2 \alpha}{\partial \xi^2} \quad (10)$$

Additionally, three boundary conditions should be introduced. One of them is based on the dimensionless Eq. (6):

$$\frac{\partial \alpha}{\partial \xi}(x, \xi = 0) = \frac{kH(1-\alpha)}{D} \quad (11)$$

Two others are expressed as Eqs. (12) and (13):

$$\alpha(x = 0, \xi) = 0 \quad (12)$$

$$\frac{\partial \alpha}{\partial \xi}(x, \xi = 1) = 0 \quad (13)$$

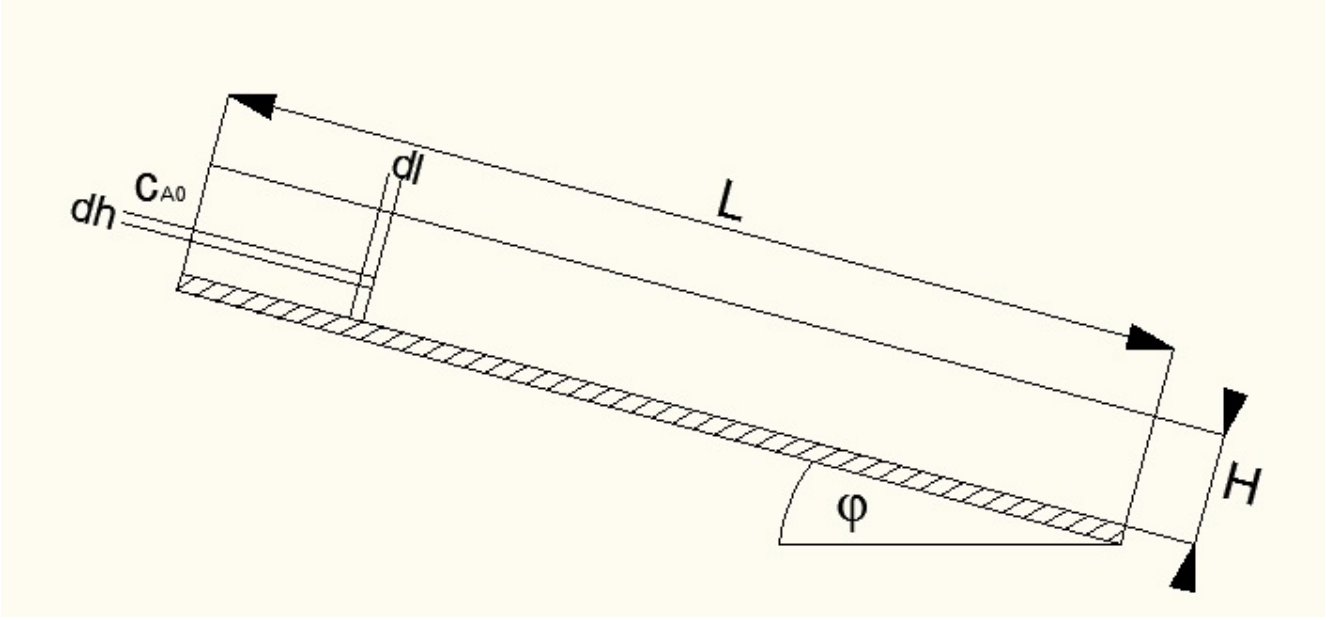

Fig. 1. Schematic drawing of the laminar gravitational liquid flow reactor with its geometrical configuration.

Next two of the earlier mentioned dimensionless numbers may be introduced. The following equations provide the final model:

$$\frac{\partial\alpha}{\partial x}=\frac{1}{\mathrm{Pe}_z}\frac{\partial^2\alpha}{\partial\xi^2} \tag{14}$$

$$\frac{\partial\alpha}{\partial\xi}\left(x,\xi=0\right)=\mathrm{Da}_{II}\left(1-\alpha\right) \tag{15}$$

Note that in the case of laminar flow, liquid velocity differs for different liquid layers. The velocity distribution equation is derived from Navier–Stokes equation; it is assumed that liquid flow is only one-dimensional and it is induced by the apparent weight of the liquid film.

$$\mu\frac{d^2U}{dh^2}=\rho g\sin\left(\varphi\right) \tag{16}$$

Two boundary conditions are applied: there is no flow on the catalyst surface (Eq. (17)) and no friction from the air (Eq. (18)).

$$U\left(h=0\right)=0 \tag{17}$$

$$\frac{dU}{dh}\left(h=H\right)=0 \tag{18}$$

The integration of Eq. (16) and introduction of the dimensionless variable Eq. (9) as well as the relation between the velocity of liquid and dimensionless height of the liquid film are emphasized.

$$U\left(\xi\right)=\left(\xi-\frac{1}{2}\xi^2\right)H^2\rho g\frac{\sin\varphi}{\mu} \tag{19}$$

If Eq. (19) will be connected to Eq. (14), therefore, Pe_z will depend on ξ. Instead, the maximal transverse Peclet number is defined as:

$$\mathrm{Pe}_{zmax}=\frac{U_{\max}H^2}{DL}=\frac{H^4\rho g\sin\varphi}{\mu DL} \tag{20}$$

Thus model Eq. (14) is modified as:

$$\left(\xi-\frac{1}{2}\xi^2\right)\frac{\partial\alpha}{\partial x}=\frac{1}{\mathrm{Pe}_{z\max}}\frac{\partial^2\alpha}{\partial\xi^2} \tag{21}$$

3. Results

Model Eq. (21) was solved by the MATLAB PDE tool in the presence of boundary conditions given by Eqs. (12), (13) and (15). Maps of the substrate conversion degree obtained in that way emphasize the limitation of mass transfer. When there is no mass transfer limitation, the map of the substrate conversion degree is as shown in Fig. 2(a). There is no difference between the degrees of substrate conversion in the vertical direction. In this case, the reactor behaves as a plug-flow tubular reactor. The situation can change with the operation parameters (as shown in Fig. 2(b)).

If the ethanol–water system is considered, the liquid film depths (for $\mu = 10^{-3}$ Pa s, $\rho = 10^3$ kg m^{-3}, $D = 10^{-5}$ m^2 s^{-1} (D is a dispersion coefficient and it is evaluated by corresponding correlation [9]; molecular diffusion coefficient is equal to 1.24×10^{-9} m^2 s^{-1}), $\varphi = 30°$, $L = 1$ m) will be equal to 670 μm and 2.1 mm for $\mathrm{Pe}_{zmax} = 0.1$ and $\mathrm{Pe}_{zmax} = 10$, respectively. It can be noticed that the change in the liquid film depth over three times affects strongly the overall effectiveness (as showed in Fig. 2).

It is hard to express the threshold transverse Peclet number for which the mass transfer limitation should be taken into account in the overall process. In this paper, we propose the following procedure:

The area of a substrate conversion degree was discretized by regular, rectangular mesh and nodes were named by each

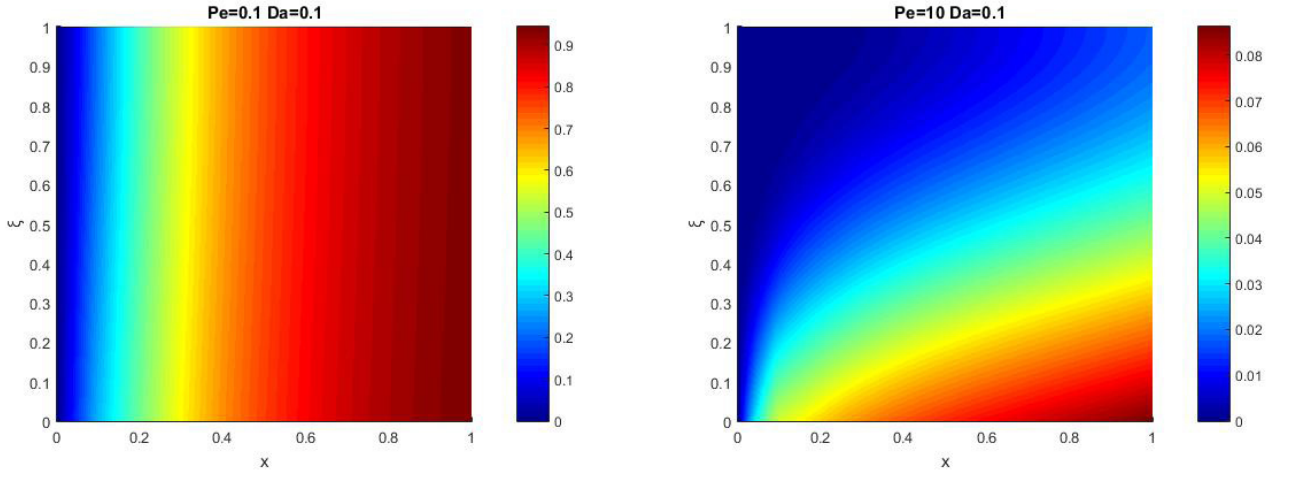

Fig. 2. Degree of substrate conversion maps: (a) process is not limited by mass transfer and (b) significant influence of mass transfer

column $i = 1, 2, \ldots, I$ and row $j = 1, 2, \ldots, J$, respectively. For each column i of the mesh data, the deviation between those values and their mean can be computed by the following equation:

$$\sigma_i = \frac{\sum_j \frac{\left|\alpha_{i\,\mathrm{mean}} - \alpha_{ij}\right|}{\alpha_{ij}}}{J} \tag{22}$$

The mean deviation for each $i = 1, 2, \ldots, I$ values was obtained by Eq. (23) and plotted in Fig. 3 for different Peclet and Damköhler numbers.

$$\sigma = \frac{\sum_i \sigma_i}{I} \tag{23}$$

The mean standard deviation values obtained by Eq. (23), starting from some Peclet number values, present a distinct trend, which could be interpreted as decreasing the importance of mass transfer influence on the overall process limitation. In this paper, we assumed that the threshold transverse Peclet number corresponds to a standard deviation equal to 5% – this value is an accuracy of popular statistical tests. The assumed threshold of mass transfer limitation lies between Pe 0.3 and 0.7. It could be noticed that the value of threshold Peclet number is constant until the second Damköhler number reaches 0.1. Over that value, the threshold Peclet number increases insignificantly. All in all, the relation between Peclet number and height of the liquid film is proportional to H^4, so the change of reaction intensification does not influence strongly the threshold-operation parameters. The point is to carry on the hydrodynamics to gain the highest process efficiency.

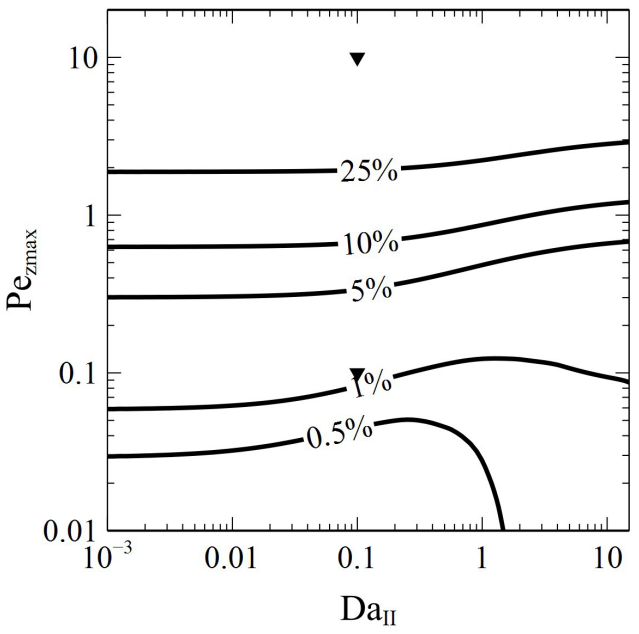

Fig. 3. Mean standard deviation of the approximation of transverse distribution of the substrate conversion degree by an average value. Solid triangles represent cases mentioned in Fig. 2.

4. Discussion

In several works, the influence of mass transfer limitation on the overall photocatalytic reaction effect is a priori neglected [10,11]. This paper shows when this assumption could be applied. It means that some kinetic works may require reconsideration. Note that a transverse threshold Peclet number remains below the value of 0.6 even for a big Damköhler number. Nevertheless, operations under those conditions should provide sufficient condition to regress experimental data to a kinetic model. Such a description of the process provides information about the rate of elementary process (here expressed by Damköhler number) and as a result, indirectly expresses the relation between the height of the liquid film and the dispersion coefficient. It could be also noticed that the obtained values of a threshold of mass transfer limitation is opposed to the above mentioned. It indicates that those studies should be also extended for reactors with flow of media in two or three dimensions (for example, for reactors with swirl flow). The model can be also used in the case of dense liquid medium – muggy suspensions or gels. Note that in such cases, the correction of Eq. (16) for non-Newtonian liquids may be needed. In addition, it is possible to describe under which condition it is most likely to gain maximal productivity. Such information can be calculated by optimization.

Symbols

a	—	Specific surface area, m^{-1}
c_{A0}	—	Initial substrate concentration, mole m^{-3}
D	—	Transverse dispersion coefficient, $m^2\ s^{-1}$
Da	—	Damköhler number
g	—	Gravitational constant, $m^2\ s^{-1}$
h	—	Height, m
H	—	Liquid-film height, m
k	—	Superficial reaction kinetics constant, s^{-1}
k_{mass}	—	Mass transfer constant, $m\ s^{-1}$
l	—	Length, m
L	—	Reactor length, m
m	—	Reaction kinetic order
Pe_z	—	Transverse Peclet number
Pe_{zmax}	—	Maximal transverse Peclet number
s	—	Reactor width, m
U	—	Liquid velocity, $m\ s^{-1}$
x	—	Dimensionless length

Greek

α	—	Degree of substrate conversion
φ	—	Slope angle of a plate
μ	—	Kinematic viscosity coefficient, Pa s
ρ	—	Density, $kg\ m^{-3}$
σ	—	Deviation
ξ	—	Dimensionless height

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