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MATHEMATICAL MODEL OF A FLAT PLATE PHOTOCATALYTIC REACTOR
IRRADIATED BY SOLAR LIGHT

MODEL MATEMATYCZNY PŁASKIEGO REAKTORA FOTOKATALITYCZNEGO,
PRACUJĄCEGO W ŚWIETLE SŁONECZNYM

Abstract

The paper presents a model of a flat plate photocatalytic reactor under solar radiation. The model was based on convection and diffusive mass flux balances in two zones: thin liquid layer and pores in the layer of a porous catalysts. The flux of light intensity was described by Kubelka–Munk theory.

Keywords: modeling, photocatalysis, reactors, solar radiation

Streszczenie

W artykule przedstawiono model opisujący pracę płaskiego reaktora fotokatalitycznego, pracującego w świetle słonecznym. Model został oparty o bilans konwekcyjnych i dyfuzyjnych strumieni masy w dwóch strefach: cienkim filmie cieczy i porach warstwy katalizatora. Strumień natężenia światła został opisany za pomocą teorii Kubelka–Munka.

Słowa kluczowe: modelowanie, fotokataliza, reaktory, promieniowanie słoneczne

1. Introduction

Advanced oxidation processes are developed as an alternative for biological water treatment [1, 2] and air pollution removal [3, 4]. Several works also present different uses of these methods: hydrogen production from water splitting and the decay of hydrogen disulfide [5]. Photocatalysis is one of the most elaborated oxidation processes due to its potentially low-cost generation in the case of carrying the process under solar radiation.

The photocatalytic potential of oxidation is generated in semiconductor catalysts. An electron from the valence band may be excited to the conduction band if there a photon is absorbed, whose energy is higher than the difference of energy between the bands, which rely on the kind of semiconductor used in the photocatalytic process.

Photocatalysis is realized in photocatalytic reactors. At present, there are two general concepts of photocatalytic reactor design. The first kind is a flat surface coated with a semiconductor layer, where only a thin film of fluid makes contact with the immobilized catalysts. The volume where the reaction takes place is limited to the immobilized catalyst layer, where the flux of radiation penetrating the catalysts is significant. The second type may be defined as a suspension of semiconductor nanoparticles in an aqueous solution of the reacting substrate. Ideal mixing in reactors guarantees bigger than immobilized reactor volume where the reaction occurs and process kinetics is not limited by diffusion. The main problems of these devices are: limited concentration of particles due to their aggregation and a separation method that is heavy to realize in continuous mode, after which the catalyst's particles cannot be used again [6]. Several cases of scaling-up the flat plate type have been reported [7]. To optimize their work, it is necessary to create a mathematical model, obtaining efficiency of the process in a wide range of parameters.

2. Basic aspects of assumptions selection

2.1. Kinetics of photocatalytic process

Most of the works the describing kinetics of photocatalytic processes use Langmuir-Hinshelwood kinetics [8, 9]. It is assumed that the oxidation center is an electron hole located on the crystal's surface, so the reaction rate has to be correlated with the adsorption equilibrium:

$$r = k_{LH} \frac{Kc}{1 + Kc} \quad (1)$$

where:

k_{LH} – is a Langmuir–Hinshelwood constant describing the rate of surface reaction;

K – is an adsorption equilibrium constant;

c – is a concentration of degraded substrate.

Apart from the reports [10, 11] indicating inaccuracies in the theory of the Langmuir–Hinshelwood model with conclusions resulting from experiments, it has been still successfully

used in kinetic data regression [8, 9]. The Langmuir–Hinshelwood model may be simplified, if $K_{\text{ads}}c \ll 1$ kinetics will gain a pseudo-first order:

$$r = k_{\text{app}}c \quad (2)$$

where:

$$k_{\text{app}} \sim Kk_{\text{LH}}$$

It is reasonable when the concentration of the decayed substance is relatively low and such assumption will be made in this paper.

The relation of the light flux intensity on the reaction rate can be described by [10]:

$$k_{\text{LH}} = k\varphi^n \quad (3)$$

where:

k – kinetic constant, related to radiation intensity is 1 Wm^{-2} ;

φ – light intensity in Wm^{-2} ;

n – parameter.

Note that n is 1 for a low intensity level and could vary with different light flux, which is accounted on limiting kinetics by mass transfer resistance [10, 12]. In this work, the linear relation between the light intensity flux and the reaction rate is approached because mass transfer resistance is considered in a different way, so that the kinetic model is modified.

$$r = \frac{k_{\text{LHodn}}I}{I_{\text{odn}}} \frac{K_{\text{ads}}c}{1 + K_{\text{ads}}c} \quad (4)$$

where:

k_{LHodn} – Langmuir–Hinshelwood constant, measured in I_{odn} light intensity;

I – light flux intensity in Wm^{-2} .

2.2. Light penetration through catalyst layer

Models describing the rate of degradation in flat plate type photocatalytic reactors [13, 14] do not consider that a photocatalytic reaction can also take part inside the catalyst layer, where the light flux penetrating the bulk catalyst can be still significant and has influence on the overall degradation effect. This work also takes into account degradation that takes place deep in catalyst pores; therefore, it is important to select the light penetration model. Recently, the Kubelka–Munk model was successfully used to describe light penetration in particulate materials [15]. The Kubelka–Munk theory considers that light is penetrating an endless plate on both sides and it changes by light absorption or scattering on penetrated media (Fig. 1). The process is described by a couple of equations, whose analytical solution is expressed as:

$$I(\lambda, \delta) = I_0(\lambda) [u(1-\beta)\exp(\alpha\delta) + v(1+\beta)\exp(-\alpha\delta)] \quad (5a)$$

$$J(\lambda, \delta) = J_0(\lambda) [u(1+\beta)\exp(\alpha\delta) + v(1-\beta)\exp(-\alpha\delta)] \quad (5b)$$

where:

I, J – light intensity flux, penetrating the mass of the penetrated substance on both sides in Wm^{-2} ;

I_0, J_0 – light flux intensity irradiated on both sides of the penetrated substance on its borders in Wm^{-2} ;

α – parameter expressed by equation (6a);

β – parameter expressed by equation (6b);

δ – depth for which the light flux intensity is expressed in m;

u, v – constants, calculated by equations (7a) and (7b);

α, β, u and v can be expressed by:

$$\alpha = \sqrt{\kappa(\kappa + 2\sigma)} \quad (6a)$$

$$\beta = \sqrt{\frac{\kappa}{\kappa + 2\sigma}} \quad (6b)$$

$$u = \frac{(\beta - 1)\exp(-\alpha\Delta)}{(1 + \beta^2)\exp(\alpha\Delta) - (1 - \beta)^2 \exp(-\alpha\Delta)} \quad (7a)$$

$$v = \frac{(\beta + 1)\exp(-\alpha\Delta)}{(1 + \beta^2)\exp(\alpha\Delta) - (1 - \beta)^2 \exp(-\alpha\Delta)} \quad (7b)$$

where:

κ – light absorption coefficient in m^{-1} ;

σ – light scattering coefficient in m^{-1} ;

Δ – depth of penetrated substance in m.

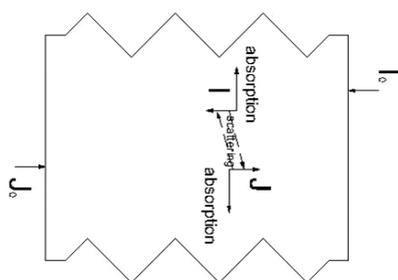


Fig. 1. Exposure of radiation stream, contributed to Kubelka–Munk equation

In this work, it is approached that a catalyst is irradiated by solar radiation only from the top, so $J_0 = 0$. As it is shown in equation (5a) and also because the light scattering and absorption coefficient can vary for different light wavelengths, one must know the spectral distribution of solar light. Work [16] presents the model based on the spectrum of solar light on a ground level. The solution may be used as I_0 in eq. (5a). Only for a part of the spectrum,

where the photon has higher energy, the excitation energy is balanced in this model. The photon energy is bonded with the wavelength by relation:

$$\lambda = \frac{hc}{E} \quad (8)$$

where:

- λ – minimal wavelength to excite electron in semiconductor in nm;
- h – Plack's constant in eVs⁻¹;
- c – velocity of light in nms⁻¹;
- E – excitation energy eV.

This means that only light, which has a wavelength lower than calculated from equation (8), can effectively excite an electron and generate a free electron – whole pair. Most of the semiconductors need radiation that has a wavelength, which corresponds to near UV radiation or lower. It constitutes about 5% of the overall solar energy in a ground level [16]. The maximal amount of energy for TiO₂ at anase, obtained from that model, is about 55 Wm⁻². It is over twice more than the one measured in the experimental work [17], when the sky is clear, probably because they take into account the slope of the plate. Apart from that, the value in outdoor conditions should be higher, because most of the UV radiation is accumulated through high scattering from the ground [16]. It is hard to obtain that effect, so that I_0 could be approached as a value received from work [16].

The scattering and absorption coefficient can vary not only with the wavelength change and with the type of catalysts. Also, the method of catalyst's synthesis may be responsible for the disagreement of the experimental results [18]. Example values were measured in work [19].

The Kubelka–Munk model equation may be simplified. By calculating u and v from equations (7) in a boundary case, when , we can get:

$$\lim_{\Delta \rightarrow \infty} u = 0 \quad (9a)$$

$$\lim_{\Delta \rightarrow \infty} v = \frac{1}{1 + \beta} \quad (9b)$$

These conditions change the form of the equation (5a) as:

$$I(\lambda, \delta) = I_0(\lambda) \exp(-\alpha\delta) \quad (10)$$

The overall light flux evaluated in the model is obtained by integration:

$$I(\delta) = \int_{\lambda=0}^{\lambda_{\min}} I(\lambda, \delta) d\lambda \quad (11)$$

The light flux, which is related to the kinetic parameters obtained in an experimental way (I_{odn}), for sure cannot be measured experimentally, because it corresponds to the fictional value of the average light flux, which may quantitatively affect such a reaction effect and it can be calculated by:

$$I_{\text{odn}} = \frac{\int_0^{\Delta} I(\delta) d\delta}{\Delta} \quad (12)$$

where:

- I_{odn} – a function, whose value can be obtained by equation (10), where I_0 equals the one measured in experiments;
- Δ – depth of layer of semiconductor.

3. Mathematical model

The model of a flat-plate photocatalytic reactor is based on the mass balance of a degraded substrate. The mass streams included in the model are schematically presented in Figure 2. The equation describing the mass balance in a differential part of liquid film is defined as:

$$shdl \frac{dc_A}{dt} = shUc_A - shU \left(c_A - \frac{dc_A}{dl} dl \right) - s dl \varepsilon k_L (c_A - c_{Ar}) \quad (13)$$

where:

- s – width of reactor plate;
- h – height of liquid film;
- U – mean velocity of liquid film;
- c_A – concentration of degraded substance;
- L – length of reactor;
- ε – catalyst layer porosity;
- k_L – overall mass transfer.

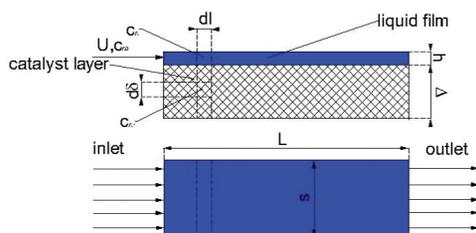


Fig. 2. Scheme of flat plate photocatalytic reactor, modeled in this work

The model also considers the equation of mass balance in an infinite volume of catalysts pores:

$$sdl \cdot \varepsilon \frac{\partial c_{Ar}}{\partial t} = -sdl \varepsilon D \frac{\partial c_{Ar}}{\partial \delta} + sdl \varepsilon D \left(\frac{\partial c_{Ar}}{\partial \delta} - \frac{\partial}{\partial \delta} \frac{\partial c_{Ar}}{\partial \delta} d\delta \right) - sdl d\delta (1-\varepsilon) \frac{k_{LHodn} I(\delta) K c_{Ar}}{I_{odn}} \quad (14)$$

where:

D – diffusion coefficient;

c_{Ar} – concentration of substrate in catalysts porous zone.

After introducing dimensionless variables, the model of the photocatalytic reactor operated under a steady state can be presented as:

$$\frac{\partial \alpha}{\partial z} = \frac{k_L \varepsilon \tau}{h} (\alpha - \alpha_r(0)) \quad (15)$$

$$\frac{\partial^2 \alpha_r}{\partial z_r^2} = \frac{(1-\varepsilon) \Delta^2}{\varepsilon D_{AB}} k_{LHodn} K \frac{I(z_r \Delta)}{I_{odn}} (1 - \alpha_r) \quad (16)$$

where:

α – dimensionless concentration of substrate in film liquid zone;

α_r – dimensionless concentration of substrate in catalysts porous zone;

z – dimensionless length of reactor;

z_r – dimensionless depth of catalysts layer.

Values α , α_r may be obtained by:

$$\alpha = \frac{c_{A0} - c_A}{c_{A0}} \quad (17)$$

$$\alpha_r = \frac{c_{A0} - c_{Ar}}{c_{A0}} \quad (18)$$

The initial condition is purposed as:

$$\alpha(0) = 0 \quad (19)$$

For equation (16), boundary conditions (20) and (21) can be applied:

$$\frac{d\alpha_r}{dz}(\delta=0) = \frac{k_L \Delta}{D_{AB}} (\alpha_r - \alpha) \quad (20)$$

$$\frac{d\alpha_r}{dz_r}(\delta=1) = 0 \quad (21)$$

4. Discussion

The presented model can obtain the work of a flat plate photocatalytic reactor under solar radiation in a wide range of process parameters. It occurred through a sacrifice of its accuracy. Other works obtain the rate of a process as a function of the energy absorbed from the light

photon flux on a photocatalytic surface. The quantity of photons reaching the catalyst surface may be used in the model as the I_0 vector in the way of different calculation, for example, the local-area-specific rate of energy absorption (LASREA) [20] or the local volumetric rate of energy absorption (LVREA) [21], as they were used in the mentioned works. Note that such a calculation can have no influence on solution accuracy in the case of processing in changing atmospheric conditions, which are not accounted on the model and may have a stronger influence on it. The solution presented in this work measures the limitation of the process rate by diffusion and that aspect can vary with the size of the reactor. It is possible that the reaction rate has also been significantly underestimated instead of the diffusive transport of the decayed substrate and radiation, penetrated inside semiconductor layer was not considered. The model can be used as the basis for the evaluation of the reactor operation under the distribution of velocity of the liquid film and concentration gradient, generated through diffuse transport in catalyst pores may be needed.

Research may be also continuing by attaching other adsorption equilibrium models (BET isotherm or Dubinin equations, referred to microporous adsorption [22]).

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