

About Microalgae Growth Kinetics Modeling

P. Popova* and Ch. Boyadjiev

Bulgarian Academy of Sciences, Institute of Chemical Engineering,
“Acad. St. Angelov” str., Bl. 103, 1113 Sofia, Bulgaria

Original scientific paper
Received: August 13, 2007
Accepted: June 30, 2008

A method for modeling microalgae growth kinetics is presented. The model parameters were obtained using experimental data for biomass concentration only. The relation between biomass concentration and CO₂ concentration in liquid phase was obtained. The proposed model is in good agreement with the experimental data. The presented method is applicable for different photosynthetic processes.

Key words:

Microalgae culture, mathematical model, airlift photobioreactor, parameter identification

Introduction

Microalgae are a natural source of high-value compounds for the pharmaceutical and food industry, such as bioactive compounds, vitamins, pigments and fatty acids.¹ In addition, in the long term, algae culture may be useful for production of clean fuels. Photosynthetic algal culture is carried out in photobioreactors that may be illuminated naturally (outdoor) or artificially (indoor). Availability and intensity of light are the major factors controlling productivity of photosynthetic cultures.²

Photobioreactors using algae, plants cells or photosynthetic bacteria have received considerable attention from biochemical engineers. Industry is presently engaged in developing new products and testing a new generation of algae-derived natural products.³

The algae near the irradiation source are exposed to high photon flux density, which enhances their growth rate. The cells at the core of the reactor receive less light as a result of mutual shading and will show a lower growth rate.^{4–7}

The process of photosynthesis can be distinguished into light and carbon-fixation reactions because they are physically separated.^{8,9} Photosynthesis is obviously linked to the availability of carbon dioxide.

Although several cell-based models of photosynthesis have been proposed,^{10–19} they consider only the light availability. These models both use classic enzyme kinetics and assume slow enzyme-controlled reactions dependent only on light to account for the carbon-fixation reactions^{10,13,16,19} or assume that photosynthetic rates are mainly related to light intensity.^{14,16,18} Other models

recognize the CO₂ dependence but ignore it in the model¹⁵ or assume that carbon fixation is proportional to the light intensity and the available carbon.²⁰

The biomass concentration increase rate is determined from the photon flux intensity and interphase mass transfer rate of CO₂. If the photon flux is a constant, the process rate depends on the CO₂ concentration in the liquid phase, i.e. from the interphase mass transfer rate in the gas-liquid system. The modeling of the photosynthetic processes in airlift reactor will be the aim of this paper.

Materials and methods

Bioprocesses modeling in an airlift reactor

Let's consider the airlift reactor for photosynthetic processes, where the interphase mass transfer of CO₂ is realized in the riser zone and the photochemical reaction in the downcomer zone. The main particularity in these cases is the low rate of photosynthetic processes. The theoretical analysis will be made based on the diffusion model of the airlift reactor.^{23,24} In case of a non-stationary process the airlift reactor can be considered as circulation tubular reactor, where the CO₂ distribution in the liquid phase is determined from convection-diffusion equation with volume reaction:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right) - kc;$$

$$t = 0, c = c_0; \quad r = 0, \frac{\partial c}{\partial r} = 0; \quad r = r_0, \frac{\partial c}{\partial r} = 0;$$

$$x = 0, c(t, r, 0) = \bar{c}(t, l), \quad \bar{u}c(t, l) = u\bar{c}(t, l) - D \frac{\partial c}{\partial x}, \quad (1)$$

*Corresponding author: Petya Popova;
Phone: (+359 2) 979-63-13; Fax: (+359 2) 8709-75-23;
E-mail: petyabs@yahoo.com

where $u(r)$ and $c(x,r,t)$ are the velocity and the concentration distribution of CO_2 in the liquid phase in the reactor, \bar{u} and \bar{c} – average velocity and concentration of CO_2 of a entrance (exit) in (out) of the reactor, D – diffusivity, k – coefficient of reaction rate, l – height of the liquid column in the reactor, r_0 – the reactor radius, t – time.

The problem (1) will be analyzed in dimensionless form, using the characteristic scale of the process:

$$\begin{aligned} t &= t_0 T, \quad x = lX, \quad r = r_0 R, \\ u &= \bar{u} U, \quad c = c_0 C, \quad \bar{c} = c_0 \bar{C}. \end{aligned} \quad (2)$$

The replacement of eq. (2) in eq. (1) leads to:

$$\frac{\partial C}{\partial T} + \frac{\bar{u} t_0}{l} u \frac{\partial C}{\partial X} = \frac{\bar{u} t_0}{l} \frac{1}{Pe} \left[\frac{\partial^2 C}{\partial X^2} + \frac{l^2}{r_0^2} \left(\frac{1}{R} \frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial R^2} \right) \right] - k t_0 C;$$

$$T=0, \quad C=1; \quad R=0, \quad \frac{\partial C}{\partial R}=0; \quad R=1, \quad \frac{\partial C}{\partial R}=0;$$

$$X=0, \quad C(T,R,0) = \bar{C}(T,1), \quad (U-l)\bar{C}(T,1) = \frac{1}{Pe} \frac{\partial C}{\partial X}, \quad (3)$$

where

$$Pe = \frac{\bar{u} l}{D}. \quad (4)$$

Non-stationarity of the process is a result of the recirculation (see the boundary conditions at $x=0$), and depends on the coefficient of reaction rate k , i.e. for characteristic time can be used:

$$t_0 = \frac{1}{k} \quad (5)$$

The replacement of eq. (5) in eq. (3) leads to:

$$\delta \left(\frac{\partial C}{\partial T} + C \right) = \frac{1}{Pe} \left[\frac{\partial^2 C}{\partial X^2} + \frac{l^2}{r_0^2} \left(\frac{1}{R} \frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial R^2} \right) \right] - u \frac{\partial C}{\partial X}, \quad (6)$$

where $\delta = \frac{kl}{\bar{u}}$ is a small parameter ($\delta \ll 1$) in cases of slow reaction rate ($k \ll 1$). That gives one possibility to find the solution of eq. (6).

$$C(T,R,X) = C_0(R,X) + C_l(T) \quad (7)$$

and from (3) and (6) is obtained:

$$\delta \left(\frac{\partial C_l}{\partial T} + C_0 + C_l \right) = \frac{1}{Pe} \left[\frac{\partial^2 C_0}{\partial X^2} + \frac{l^2}{r_0^2} \left(\frac{1}{R} \frac{\partial C_0}{\partial R} + \frac{\partial^2 C_0}{\partial R^2} \right) \right] - u \frac{\partial C_0}{\partial X},$$

$$T=0, \quad C_0=0, \quad C_l=1; \quad R=0, \quad \frac{\partial C_0}{\partial R}=0; \quad R=1, \quad \frac{\partial C_0}{\partial R}=0;$$

$$X=0, \quad C_0(R,0) = C_0(1), \quad (U-1)(\bar{C}_0(1) + \bar{C}_l(1)) = \frac{1}{Pe} \frac{\partial C_0}{\partial X}. \quad (8)$$

The solution for $C_0(R,X)$ can be obtained from eq. (8) in zero approximation of parameter δ :

$$u \frac{\partial C_0}{\partial X} = \frac{1}{Pe} \left[\frac{\partial^2 C_0}{\partial X^2} + \frac{l^2}{r_0^2} \left(\frac{1}{R} \frac{\partial C_0}{\partial R} + \frac{\partial^2 C_0}{\partial R^2} \right) \right];$$

$$X=0, \quad C_0(R,0) = 0, \quad \frac{\partial C_0}{\partial X} = 0.$$

$$R=0, \quad \frac{\partial C_0}{\partial X} = 0; \quad R=1, \quad \frac{\partial C_0}{\partial X} = 0. \quad (9)$$

The boundary conditions in (9) at $X=0$ follow from volume reaction absence ($\frac{\partial C_0}{\partial X} = 0$) and initial condition at $T=0$ ($C_0=0$). At these conditions the solution of eq. (9) is $C_0(R,X) \equiv 0$, that permits to obtain $C_l(T)$:

$$\frac{\partial C_l}{\partial T} = -C_l, \quad T=0, \quad C_l=1; \quad (10)$$

from where:

$$C_l = e^{-T}. \quad (11)$$

This result shows that for slow volume reactions the process rate is determined from their kinetics and the column (airlift) reactor exercises the function of apparatus with ideal mixing regime. Thus, the photosynthetic process model in airlift reactor is reduced to model of photosynthetic kinetics.

Mathematical model

The experimental data for increasing the microalgae (*Porphyridium* sp) concentration with time (the points in Figs. 1, 3, 5) lead to the hypothesis that the growth mechanism comprises two processes whose rates level off in the course of time, and the concentration of microalgae becomes steady.

The kinetic equation corresponding to this mechanism has the form:

$$\frac{dc_x}{dt} = \mu_{\max} \frac{c}{k_1 + c} c_x - k_0 c_x, \quad (12)$$

where $c_x = c_x(t)$, $c = c(t)$.

Porphyridium sp was grown in artificial seawater.²⁵ Air enriched with $w = 3\%$ CO_2 was sparged into the reactor. A bank of fluorescent lamps was used as illumination source giving photon flux density $250 [\mu\text{E m}^{-2} \text{s}^{-1}]$. All experiments were carried out in a room with controlled temperature ($23\text{--}25^\circ\text{C}$).²

The experiments of cultivation of *Porphyridium sp* were carried out in a laboratory tubular device in an airlift photobioreactor of 13 dm³ volume²⁶ in conditions close to the ideal mixing regime in liquid phase.

The CO₂ concentration changes with time $c(t)$ independence of the balance of the rate of CO₂ consumption for biomass growth and the interphase mass transfer rate in the gas phase.

$$\frac{dc}{dt} = Q - A_x \mu_{\max} \frac{c}{k_1 + c} c_X. \quad (13)$$

The volumetric mass transfer rate Q can be determined by the average CO₂ concentration in the gas phase of input and output from the column:

$$Q = \frac{u}{h} (c_{0,gas} - c_{h,gas}). \quad (14)$$

The overall mass transfer rate Q depends on the local mass transfer rate q of column height.

$$Q = \frac{1}{h} \int_0^h q dc_X, \quad (15)$$

where

$$q = k(c_{gas} - k_H c). \quad (16)$$

Assuming that the CO₂ concentration in the gas phase is changing linearly of the column height from $c_{gas}(0, t) = c_{0,gas}$ to $c_{gas}(h, t) = c_{h,gas}$:

$$c_{gas} = c_{0,gas} - \frac{k_H}{h} (c_{0,gas} - c_{h,gas}). \quad (17)$$

Putting c into (15, 16) leads to:

$$Q = k \left(\frac{c_{0,gas} + c_{h,gas}}{2} - k_H c \right). \quad (18)$$

The expressions for Q (14, 18) allow determination of the average CO₂ concentration in the gas outlet.

$$c_{h,gas} = \frac{\left(\frac{u}{h} - \frac{k}{2} \right) c_{0,gas} + k k_H c}{\frac{u}{h} + \frac{k}{2}}. \quad (19)$$

The process model is represented by (12), (13), (14) and (19) with the following boundary conditions:

$$t = 0, \quad c_X = c_{X_0}, \quad c = c_0, \quad (20)$$

where X_0 is an initial biomass concentration, $c_0 = c_{0,gas}/k_H$ if the process starts with the illumination start.

This model is characterized by 4 parameters that can be obtained from the experimental data.

Results

A previous study²⁰ showed that in cases of models with many equations and parameters, the least square function is frequently multiextremal or “ravine” type. Therefore, very good initial parameter value for determining the coefficients is needed.

For that purpose the parameters were obtained ahead in the separate equations, where the unknown functions were substituted (replaced) for polynomial approximation of the experimental data.

In the present work, substitution is difficult, because there are published experimental data for the biomass concentration only.

As it was demonstrated in the previous study²⁰ the experimental data of the concentration will be used ahead by its polynomial approximation.

$$c_X(t) = P(t), \quad \frac{dc_X}{dt} = \frac{dP}{dt} = P'(t), \quad A(t) = \frac{P'(t)}{P(t)}. \quad (21)$$

The lack of experimental data of the concentration for $c(t)$ will be substituted from “experimental data” $\hat{c}(t)$ that is obtained by eq. (1) after entering the eq. (10):

$$\hat{c}(t) = \frac{k_l [k_0 + A(t)]}{\mu_{\max} - k_0 - A(t)} \quad (22)$$

The “experimental data” $\hat{c}(t)$ is obtained from the experimental data for the biomass (microalgae), but it is conditional because it depends on several parameters μ_{\max} , k_0 , k_1 that are the subject of determination.

For model parameters identification the least square function is used.

$$F = \sum_{i=1}^N [c_X(t_i) - c_{X_{exp}}(t_i)]^2 + \alpha \sum_{i=1}^N [c(t_i) - \hat{c}(t_i)]^2, \quad (23)$$

where $t_i (i = 1, \dots, N)$ are the times in which the biomass is quantified, $\alpha = 10 \div 100$ is a specific weight that compensates the differences in the orders of the two sums.

Solving the model (12), (13), (18) and (19) at the given parameter values μ_{\max} , k_0 , k_1 is needed for determining the function F .

The boundary conditions (20) are replaced with:

$$t = 0, \quad c_{X_0} = c_{X_{\text{exp}}}, \quad c_0 = \frac{k_1 A(0)}{\mu_{\text{max}} - A(0)}, \quad (24)$$

where it is supposed that in the beginning of the process the effect of the second term in eq. (12), i.e. k_0 can be ignored.

The experimental data for the biomass shows that for $t \geq t_N$, $c_X = c_{X_N}$, $\frac{dc_X}{dt} = 0$ and from eq. (12) follows:

$$c_N = c(t_N) = \frac{k_0 k_1}{\mu_{\text{max}} - k_0} = \text{const.} \quad (25)$$

At this condition ($t \geq t_N$) $\frac{dc}{dt} = 0$, i. e.

$$\frac{u}{h}(c_{0,\text{gas}} - c_{h,\text{gas}}(t_N)) - A_X \mu_{\text{max}} \frac{c_N}{k_1 + c_N} c_{X_N} = 0, \quad (26)$$

where

$$c_{h,\text{gas}}(t_N) = \frac{c_{0,\text{gas}} \left(\frac{u}{h} - \frac{k}{2} \right) + k k_H c_N}{\frac{u}{h} + \frac{k}{2}}. \quad (27)$$

The replacement of eq. (25) in eqs. (26), (27) and subsequently of eq. (27) in eq. (26) leads to an equation that represents the relationship between the parameters μ_{max} , k , k_0 , k_1 . The latter enables determination of k as a function of the other parameters:

$$k = \frac{2u A_X c_{X_N} k_0 (\mu_{\text{max}} - k_0)}{2u(c_{0,\text{gas}} \mu_{\text{max}} - c_{0,\text{gas}} k_0 - k_H k_0 k_1) - A_X h c_{X_N} k_0 (\mu_{\text{max}} - k_0)}. \quad (28)$$

The replacement of eq. (28) in eq. (29) leads to a model with three parameters where the least square function (23) depends on the parameters μ_{max} , k_0 , k_1 .

The determination of the model parameters was made by minimization of (23) using the procedure *fminsearch* of MATLAB 6.5.

This resulted in:

$$\begin{aligned} \mu_{\text{max}} &= 0.73859 \text{ h}^{-1}, \quad k = 2.4999 \text{ h}^{-1}, \\ k_0 &= 0.01095 \text{ h}^{-1}, \quad k_1 = 0.27149 \text{ kg m}^{-3}, \quad (29) \\ F &= 0.8116 \end{aligned}$$

A test for the correctness of the inverse identification problem²¹ was made.

Therefore, the polynomial $P(t)$ in eq. (21) was used for obtaining the other “experimental data” for the biomass. Solving the inverse problem on hand of this new data set leads to:

$$\mu_{\text{max}} = 0.91956 \text{ h}^{-1}, \quad k = 2.817 \text{ h}^{-1},$$

$$k_0 = 0.01218 \text{ h}^{-1}, \quad k_1 = 0.25239 \text{ kg m}^{-3}, \quad (30)$$

$$F = 0.8449.$$

Demonstrated by the minimization procedure were the small differences between eq. (29) and eq. (30), indicating that the inverse problem is correct; i.e. the solution of the problem is not sensibility with respect to the experimental data errors.

The use of eq. (28) simplified the solution of the problem, but this eq. (28) is derived from the hypothesis that $\frac{dc_X}{dt} = 0$ for $t \geq t_N$. Thus, eq. (28) can be accepted as an approximation.

The coefficient k can be obtained more accurately by minimization of F as a function of four parameters using eq. (29) as a zero approximation. The result is:

$$\mu_{\text{max}} = 0.93139 \text{ h}^{-1}, \quad k = 2.7417 \text{ h}^{-1},$$

$$k_0 = 0.01127 \text{ h}^{-1}, \quad k_1 = 0.06419 \text{ kg m}^{-3}, \quad (31)$$

$$F = 0.7213,$$

i.e. this solution can be regarded as more precise given the value of F being less than in eq. (29).

Discussion

Gas velocity is the most important variable in pneumatic reactor operation. The amount of gas supplied to the reactor strongly influences the mixing of medium, the distribution of cells in the reactor, nutrient availability to cells, and absorption of carbon dioxide. Increased gas velocity improves mixing and therefore mass transfer.^{2,22}

Intensification of growth with increasing gas velocity can be explained by improvement of mass transfer in the reactor. The interphase mass transfer is obviously very important, since it is responsible for the provision of the CO_2 required as building blocks for the cells' growth. This step is relatively fast due to the high solubility of CO_2 in the gas used. Within the liquid itself, far from the gas-liquid interface, two mechanisms of mass transfer can be distinguished. The first is convective transfer that takes place throughout the reactor and is related to the total liquid circulation and macro-mixing. This is a function of reactor design, physical properties of the medium and gas flow rate. The second is the transfer from the bulk of the liquid toward the suspended cells.²

Liquid-cell mass transfer was influenced by the liquid properties and fluid dynamics, and depends also on cell aggregation.

The comparison between the model, with calculated parameters (see Table 1), and the experimental data for different superficial gas velocity is shown in the Figs. (1–6).

Table 1 shows the model parameter values and the values of the least square function (F).

Table 1 – The model parameter values and the values of the least square function for different superficial gas velocity

| Superficial gas velocity $u/\text{m h}^{-1}$ | Model parameter values |
|---|---|
| 1.944 | $\mu_{\max} = 1.0185 \text{ h}^{-1}$ $k_0 = 0.0094 \text{ h}^{-1}$ $k_1 = 0.0177 \text{ kg m}^{-3}$ $k = 3.7282 \text{ h}^{-1}$ $F = 0.281$ |
| 5.76 | $\mu_{\max} = 0.93139 \text{ h}^{-1}$ $k_0 = 0.01127 \text{ h}^{-1}$ $k_1 = 0.06419 \text{ kg m}^{-3}$ $k = 2.7417 \text{ h}^{-1}$ $F = 0.7213$ |
| 11.88 | $\mu_{\max} = 0.45007 \text{ h}^{-1}$ $k_0 = 0.00805 \text{ h}^{-1}$ $k_1 = 0.7758 \text{ kg m}^{-3}$ $k = 1.6004 \text{ h}^{-1}$ $F = 1.304$ |

Assuming that the gas velocity does not influence essentially the coefficients μ_{\max} , k_0 , k_1 , we can calculate their average values $\bar{\mu}_{\max}$, \bar{k}_0 , \bar{k}_1 from the three given superficial gas velocities. Then on hand of the averages we can minimize the least square function (F) in order to determine mass transfer coefficient (\bar{k}).

$$\begin{aligned} \bar{\mu}_{\max} &= 0.9749 \text{ h}^{-1}; \quad \bar{k}_0 = 0.0104 \text{ h}^{-1}; \\ \bar{k}_1 &= 0.041 \text{ kg m}^{-3} \end{aligned} \quad (32)$$

The obtained results show a dependence of the mass transfer coefficient on the superficial gas velocity:

$$k = 5286 u^{-0.3811} \quad (33)$$

The “experimental data” for $c(t)$ is obtained from eq. (22) with parameter values given in Table 1.

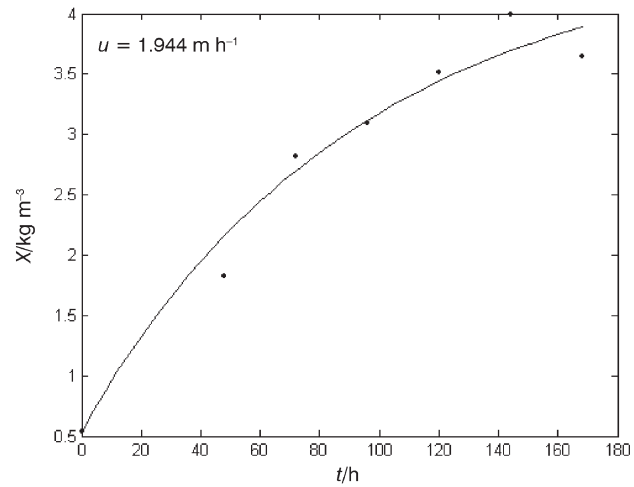


Fig. 1 – Comparison of the calculated values and experimental data for biomass concentration

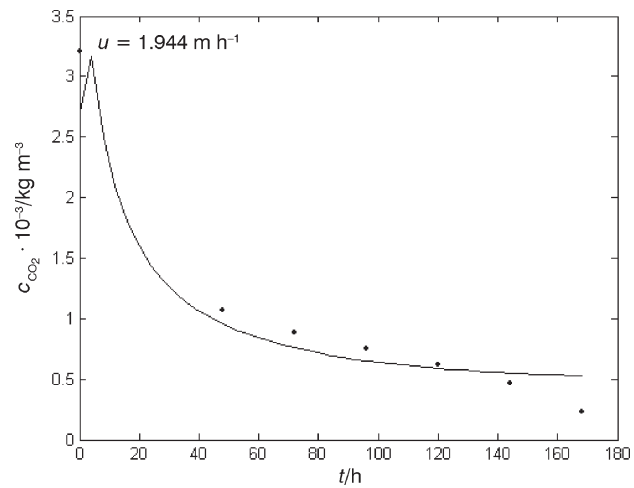


Fig. 2 – Comparison of the calculated values and experimental data for CO_2 concentration in the liquid phase

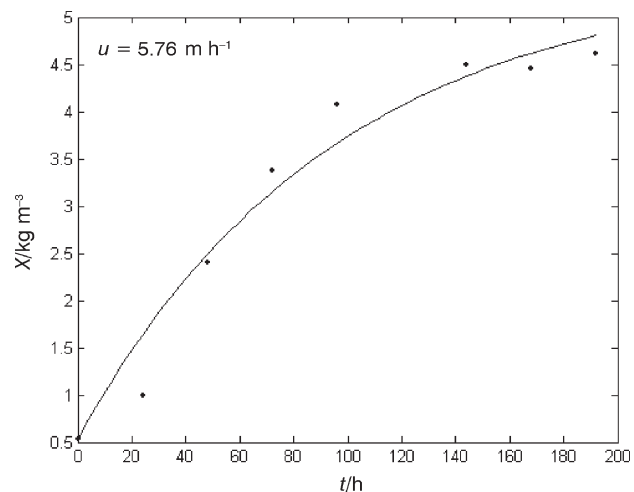


Fig. 3 – Comparison of the calculated values and experimental data for biomass concentration

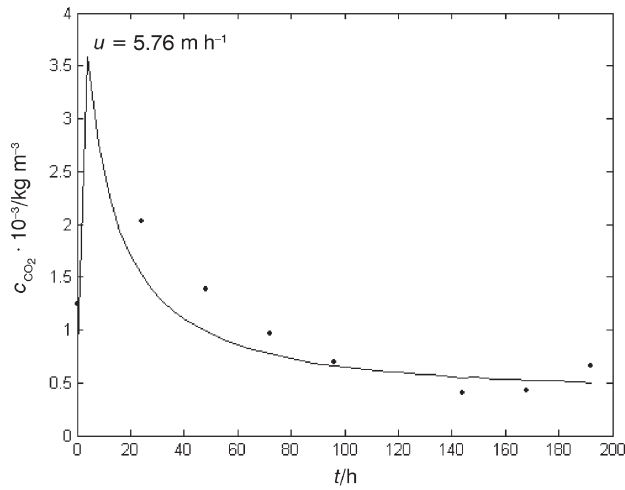


Fig. 4 – Comparison of the calculated values and experimental data for CO_2 concentration in the liquid phase

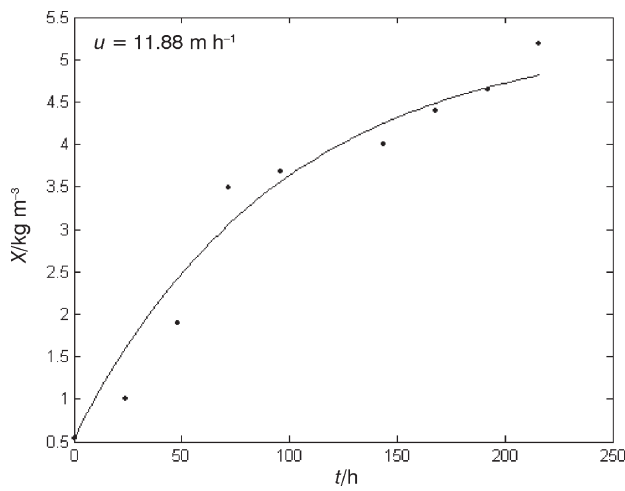


Fig. 5 – Comparison of the calculated values and experimental data for biomass concentration

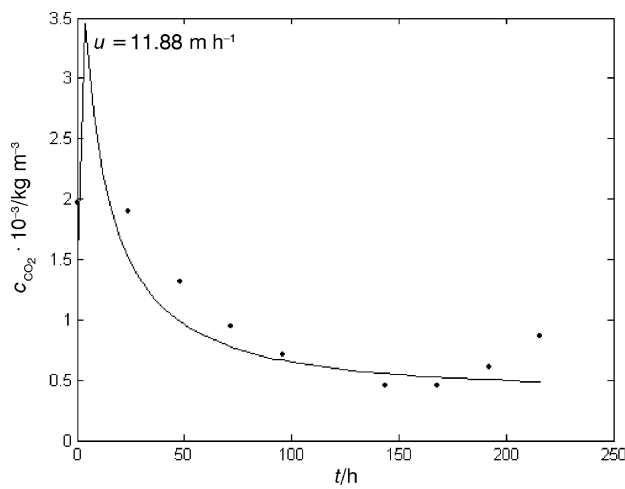


Fig. 6 – Comparison of the calculated values and experimental data for CO_2 concentration in the liquid phase

The proposed parameter identification method offers one possibility for finding a solution of a problem connected with insufficient experimental information.

The comparison of the theoretical and experimental data in Figs. (1–6) shows that the accuracy of the solution could be increased more detailed experimental data for the beginning of the process $0 \leq t \leq 24$ h is available.

The good accordance between model and experimental data confirms the hypothesis that the growth mechanism comprises two processes whose rates level off in the course of time, and the concentration of biomass becomes steady. Based on the existence of a relationship between concentration of biomass and the CO_2 concentration in the liquid phase it is demonstrated that substitution of missed experimental data with a “provisional experimental data set” is possible. The last set depends on the model parameters.

Proof for the correctness of the inverse identification problem is derived.

The presented method is applicable for different photosynthetic processes.

ACKNOWLEDGEMENTS

This work was completed with the financial support of the National Science Fund, Ministry of Education and Science, Republic of Bulgaria, index contract No. TH-1506/2005.

Nomenclature

- c_{gas} – carbon dioxide concentration in the gas phase, kg m^{-3}
- c – carbon dioxide concentration in the liquid phase, kg m^{-3}
- h – column height, m
- k – coefficient of reaction rate, h^{-1}
- k_0 – non-growth coefficient, h^{-1}
- k_l – Monod’s carbon dioxide limitation constant, kg m^{-3}
- k_H – Henry’s constant
- D – diffusivity, $\text{m}^2 \text{s}^{-1}$
- F – least square function
- N – number of the experimental data
- Pe – Peclet number, –
- Q – overall mass transfer rate, $\text{kg m}^{-3} \text{h}^{-1}$
- r, r_0 – the reactor radius, m
- l – height of the liquid column in the reactor, m
- q – local mass transfer rate, $\text{kg m}^{-3} \text{h}^{-1}$
- t – time, h
- c_X – dry biomass concentration, kg m^{-3}

- $c_{X_{\text{exp}}}$ – experimental data for dry biomass concentration,²
kg m⁻³
 u – superficial gas velocity, m h⁻¹
 w – mass fraction, %
 μ_{max} – maximum specific growth rate, h⁻¹

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