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Novel simulation model of BIOCOIL photobioreactors for CO_2 sequestration

Alessandro Concas[1], Massimo Pisu[1] and Giacomo Cao[1,2]

[1] CRS4, Center for Advanced Studies, Research and Development in Sardinia Parco Scientifico e Tecnologico, Edificio 1, 09010 PULA (CA - Italy)
[2] Dipartimento di Ingegneria Chimica e Materiali and Unità di Ricerca del Consorzio Interuniversitario Nazionale "La Chimica per l'Ambiente" (INCA), Piazza d'Armi, 09123 Cagliari, Centro Interdipartimentale di Ingegneria e Scienze Ambientali and Laboratorio di Cagliari del Consorzio INCA, Via San Giorgio 12, 09124 Cagliari, Unità di Ricerche del Dipartimento Energia e Trasporti del Consiglio Nazionale delle Ricerche, Piazza d'Armi, 09123 Cagliari, Italy

1. Introduction

The production of biofuels from algal biomass is one of the most ambitious task to fulfill a sustainable ecological balance worldwide. The main goal is the reduction of environmental contamination by recycling part of the CO_2, produced through energy generation by fossil fuels and use it for bio-oil production. Recently, the possibility of employing photoautotrophic microalgae that utilize CO_2 as a carbon source for their growth, and the subsequent production of biofuels from the obtained algal biomass, has been investigated (Chisti, 2007). From this point of view, the cultivation of cyanobacteria such as Spirulina platensis allows one to produce valuable biomass, using industrial CO_2 as carbon source (Soletto et al., 2008). It is then required to develop suitable processes which make use of selected algal species operating inside specific photobioreactors which represent the core step of the entire process. The optimal design of photobioreactors may be accomplished using suitable mathematical models. So far the models available in the literature have been able to represent the basic characteristics of algal kinetics (Molina et al., 2001). However, the behaviour of photosynthetic cultures is rather complicated since involves cell metabolism, growth and loss processes which are strongly cell size-dependent (Banse, 1976; Yang et al., 2006). Therefore this latter aspect cannot be missed when developing suitable mathematical models. In the present work we propose a novel simulation model to quantitatively describe the growth of microalgae in a re-circulating helical photobioreactor (BIOCOIL). The model accounts for "mass structured" population balances which permit to properly simulate cell growth, replication and its distribution within the tubular-helical photobioreactor. Light intensity distribution within the culture medium is also taken into account. Model results and literature experimental data (Travieso et al., 2001) in terms of dry biomass contents and its distribution within the photobioreactor tube have been successfully compared, thus demonstrating the validity of the proposed model as well as its predictive capability.

2. Mathematical modelling

The BIOCOIL photobioreactor, schematically illustrated in Figure 1, consists of several sections of PVC tubing that is wound horizontally around a vertical, cylindrical wire frame. It may be illuminated either by sunlight or fluorescent lights. Microalgal cells,

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are suspended in a liquid medium (broth) where all the nutrients, such as nitrates, phosphates and others, are previously dissolved. Liquid circulation is assured by an airlift where the flue gas containing CO_2 is bubbled in the broth thus allowing the uplifting of the liquid.

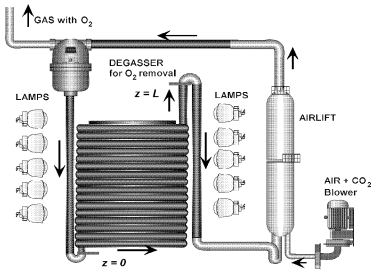

Fig. 1. Schematic representation of BIOCOIL photobioreactor

The continuous supply of carbon dioxide in the airlift avoids that carbon limitations may take place during microalgal growth. Other nutrients are not integrated during the process. The approach to simulate the growth of microalgae is based upon the classical homogeneous isothermal, axial dispersion model for main nutrient species (*C*, *N*, *P*) and photosynthesis product (O_2) present in the liquid phase. It is worth noting that micro-algae may use as carbon source both the dissolved CO_2 or HCO_3^- and CO_3^{2-} that are in the liquid medium. Since experimental data (Travieso et al., 2001) were obtained from trials where concentration of HCO_3^- and CO_3^{2-} dissolved in the broth was very high and the consumed carbon was reintegrated by the dissolution of gaseous CO_2 in the airlift system, carbon was not considered as limiting nutrient in our model. Furthermore, we assume that all photosynthetic O_2 within the degasser is removed so that the liquid recirculated in the tubular stage (light collector) does not contain O_2. Under these assumptions, and considering the tubular geometry of the photobioreactor the relevant material balances of our model may be written as follows:

$$\frac{\partial C_j}{\partial t} = -v_z \cdot \frac{\partial C_j}{\partial z} + D_z \cdot \frac{\partial^2 C_j}{\partial z^2} - \frac{1}{y_{X/j}} \int_0^{\infty} v_m\left(m, z, I, C_j, C_{O_2}\right) \cdot \psi\left(m, z\right) \cdot dm \tag{1}$$

$j = 1,..2; \quad 1 = NO_3^-; \quad 2 = H_2PO_4^-$

along with the following initial and boundary conditions:

$$C_j = C_j^0 \qquad @ \qquad t = 0,\ \forall z \in [0, L] \text{ for } j = 1,2 \tag{2}$$

$$v_z C_j - D\frac{\partial C_j}{\partial z} = v_z C_j^{z=L} \qquad @ \qquad \forall t > 0,\ z = 0 \text{ for } j = 1,2 \tag{3}$$

$$\frac{\partial C_j}{\partial z} = 0 \qquad @ \qquad \forall t > 0,\ z = L \text{ for } j = 1,2 \tag{4}$$

The material balance for oxygen may be expressed as follows:

$$\frac{\partial C_{O_2}}{\partial t} = -v_z \cdot \frac{\partial C_{O_2}}{\partial z} + D_z \cdot \frac{\partial^2 C_{O_2}}{\partial z^2} + \frac{1}{y_{X/O_2}} \int_{m_1}^{m_{\max}} v_m\left(m, z, I, C_j, C_{O_2}\right) \cdot \psi\left(m, z\right) \cdot dm \tag{5}$$

along with the following initial and boundary conditions:

$$C_{O_2} = C_{O_2}^0 = 0 \qquad @ \qquad t = 0,\ \forall z \in [0, L] \tag{6}$$

$$v_z C_{O_2} - D\frac{\partial C_{O_2}}{\partial z} = 0 \qquad @ \qquad \forall t > 0 \quad ,\ z = 0 \tag{7}$$

$$\frac{\partial C_{O_2}}{\partial z} = 0 \qquad @ \qquad \forall t > 0,\ z = L \tag{8}$$

where v_z and D_z are the liquid velocity and axial dispersion, respectively, while $y_{X/j}$ are the yields of biomass production with respect to *j-th* component consumed/ produced (i.e. weight of dry biomass produced for weight of *j* consumed/produced). The nutrients, i.e. NO_3^- and $H_2PO_4^-$, are recirculated at the photobioreactors entrance, as indicated by the boundary condition of equation 3. In the reactive term of equations (1) and (5), the time rate of change of the mass *m* for a single microalgal cell, v_m may be expressed (Mantzaris et al., 1999) as a product of the cell mass and a certain function of the limiting nutrient concentration (C_j), the photosyntetically active radiation (*I*), and the dissolved oxygen concentration. According to the Liebig's law for multiple nutrient limitation (Legovic and Cruzado, 1997) it has been expressed as follows by accounting for the equation proposed by Molina et al. (1994), being the inhibitory effect of dissolved oxygen taken from Li et al. (2003):

$$v_m\left(m,z,I,C_j,C_{O_2}\right)=\left[\mu_{\max}\cdot\frac{I^n}{I_K^n+I^n}\cdot\prod_{j=1}^{2}\frac{C_j}{K_j+C_j}\cdot\left(1-\frac{C_{O_2}}{C_{O_2,\max}}\right)-\mu_c\right]\cdot m \tag{9}$$

where μ_{max} is the maximum growth rate of microalgae, I_K is the half saturation constant for light intensity, K_j is the half saturation constant for the generic nutrient *j* and $C_{O2,max}$ is the highest concentration of dissolved oxygen at which the growth of algae is inhibited. Finally, μ_c is the catabolic rate constant which, due to the lack of information available in the literature, has been assumed equal to zero during the simulations. The average light intensity *I* within the culture is a function of biomass concentration (*X*) and for tubular photobioreactors may be expressed as follows (Molina et al., 2001):

$$I=I\left(t,z\right)=\frac{I_0\left(t\right)}{\phi_{eq}K_aX\left(t,z\right)}\cdot\left[1-\exp\left(-\phi_{eq}K_aX\left(t,z\right)\right)\right] \tag{10}$$

where ϕ_{eq} is the length of light path that is related with the tube diameter as shown by Molina et al. (2001), K_a is the optical extinction coefficient for biomass, and I_0 is the incident light intensity. To estimate the biomass concentration, the following "mass structured" population balance (Himmelblau and Bischoff, 1968) may be accounted for:

$$\frac{\partial\psi}{\partial t}=-v_z\cdot\frac{\partial\psi}{\partial z}+D_z\cdot\frac{\partial^2\psi}{\partial z^2}-\frac{\partial\left(v_m\cdot\psi\right)}{\partial m}+\Gamma\left(m,z,I,C_j,C_{O_2}\right)\cdot\psi \tag{11}$$
$$-2\int_m^\infty\psi\cdot\Gamma\left(m',z,I,C_j,C_{O_2}\right)\cdot p\left(m,m'\right)\cdot dm'$$

along with the following initial and boundary conditions:

$$\psi\left(m,z,t\right)=\psi^0\left(m,z,0\right) \qquad @ \qquad t=0,\ \forall z\in\left[0,L\right] \tag{12}$$

$$v_z\cdot\psi-D\cdot\frac{\partial\psi}{\partial z}=v_z\cdot\psi^{z=L} \qquad @ \qquad \forall t>0,\ z=0 \tag{13}$$

$$\frac{\partial\psi}{\partial z}=0 \qquad @ \qquad \forall t>0,\ z=L \tag{14}$$

where Ψ represents the cell mass distribution and v_m the time rate of change for the microalgal cell of mass *m*. The fraction of dividing cells of mass *m'* (Γ), and the probability partition function for dividing cells (*p*) may be expressed as follows (Mantzaris et al, 1999):

$$\Gamma\left(m,z,I,C_j,C_{O_2}\right)=v_m\left(m,z,I,C_j,C_{O_2}\right)\cdot\frac{\frac{1}{\sqrt{2\pi\sigma^2}}\exp\frac{-\left(m-\mu_o\right)^2}{2\sigma^2}}{1-\int_0^m\frac{1}{\sqrt{2\pi\sigma^2}}\exp\frac{-\left(m'-\mu_o\right)^2}{2\sigma^2}\cdot dm'} \tag{19}$$

$$p(m,m') = \frac{1}{\beta(q,q)} \frac{1}{m'} \left(\frac{m}{m'}\right)^{q-1} \left(1 - \frac{m}{m'}\right)^{q-1} \quad (20)$$

where σ and μ_0 are the standard deviation and the average cellular mass of dividing cells of the division probability density function, respectively, while $\beta(q,q)$ is the symmetric beta function. The solution of the population balance equation coupled with the initial and boundary conditions, for each of the axial grid point, gives the distribution of the cells and may be used to estimated the local biomass concentration X, required by the diffusion reaction equations, through the following expression:

$$X(t,z) = \int_0^\infty \psi(m,z) \cdot m \cdot dm \quad (21)$$

The numerical solution adopted to solve the proposed model is not reported for the sake of brevity.

3. Results and discussion

The proposed mathematical model has been tested by comparison with literature experimental data concerning the growth of the cyanobacteria Spirulina Platensis on "BIOCOIL" photobioreactor (Travieso et al., 2001). Spirulina Platensis has been cultured in a culture medium where all macro-nutrients (N, P) were in concentrations sufficient to sustain the batch microalgal growth for about 15 days. In particular Na_2CO_3 was present in the medium at high concentration so that no limitations due to carbon depletion may take place. In addition, the continuous supply of air enriched with CO_2 (4%) in the airlift avoided any carbon limitation during the growth rate. The BIOCOIL photobioreactor has a cylindrical shape (0.9 m high) with a 0,25 m^2 basal area and a photostage comprising 60 m of transparent PVC tubing of 1.6 cm inner diameter. The inner surface of the cylinder was illuminated with fluorescent lamps witch guaranteed a incident light intensity of about 156.64 μE m^{-2} s^{-1}. The flow-rate in tubing was equal to 19,28 cm s^{-1} (Travieso et al., 2001). The other model parameters, whose values are reported in Table 1, are taken from the literature related to either the original work from which the experimental data have been generated or to specific sources where new model parameters values are available.

Table 1 Model parameters used for simulation of Spirulina growth in Biocoil photobioreactors.

Parameter	Value	Unit	Reference
K_a	0,15	m^2 g^{-1}	Cornet et al., 1995
I_k	160	μE m^{-2} s^{-1}	Vonshak 1997
n	1,49	-	Molina et al., 2001
μ_{max}	0,52	day^{-1}	Baldia et al., 1991a
K_{NO3}	5,314	mg_{NO3} L^{-1}	Calculated from Baldia et al., 1991a.
K_{H2PO4}	0,028	mg_{H2PO4} L^{-1}	Calculated from Baldia et al., 1991b
$C_{O2,max}$	47,9	mg L^{-1}	Li et al., 2003
ρ_{cell}	1,02	g cm^{-3}	Smayda and Boleyn, 1965
$y_{X/NO3}$	2,252	g g_{NO3}^{-1}	Calculated from Paille et al., 2000
$y_{X/H2PO4}$	40,805	g g_{H2PO4}^{-1}	Calculated from Paille et al., 2000
$y_{X/O2}$	0,534	g g_{O2}^{-1}	Calculated from Paille et al., 2000
q	40	-	Mantzaris et al., 1999
μ_0	0,26	ng	This work
σ	0,125	ng	Mantzaris et al., 1999

All the parameter used in the simulation are related to microalga Spirulina Platenis. Only the coefficient n and the maximum allowed O_2 concentration ($C_{O2,max}$) were related to other microalgae. As for as the yields of nutrients $y_{x/j}$, the corresponding values are

obtained by the average stoichiometry for Spirulina platensis proposed by Paille et al. (2000). The initial mass distribution of cells was calculated by considering that typical Spirulina Platensis tricomes are constituted by a sequence of cylindrical shaped cells having diameter ranging from 4 to 12 μm with a mean value of 8 μm. The cell length varies from 2-3 with a mean value of 2,5 μm (Vonshak, 1997). By considering a specific mass of the single cell of 1,02 g cm^{-3}, a mean cell mass value of 0,128 ng was calculated along with its standard deviation. Thus, the initial mass distribution (assuming a typical Gaussian behaviour) was evaluated through the equation 21 to obtain the total initial biomass concentration reported by Travieso (250 mg L^{-1}). As for as the other parameters, the average mass of dividing cells, μ_0, appearing in Eq. (19), is assumed equal to about twice the value of the mode of the initial distribution (i.e. 0.26 ng). This seems a reasonable choice (cf. Mantzaris et al., 1999). Regarding the other parameters related to the division probability density and partitioning functions, i.e., σ and q, respectively, we select typical values for mass-structured cell population balance models in an environment of changing substrate concentrations (cf. Mantzaris et al., 1999). In Figure 1-a, model predictions, in terms of biomass concentration as a function of time at the final section of the tube, are compared with the experimental data by Travieso et al. (2001).

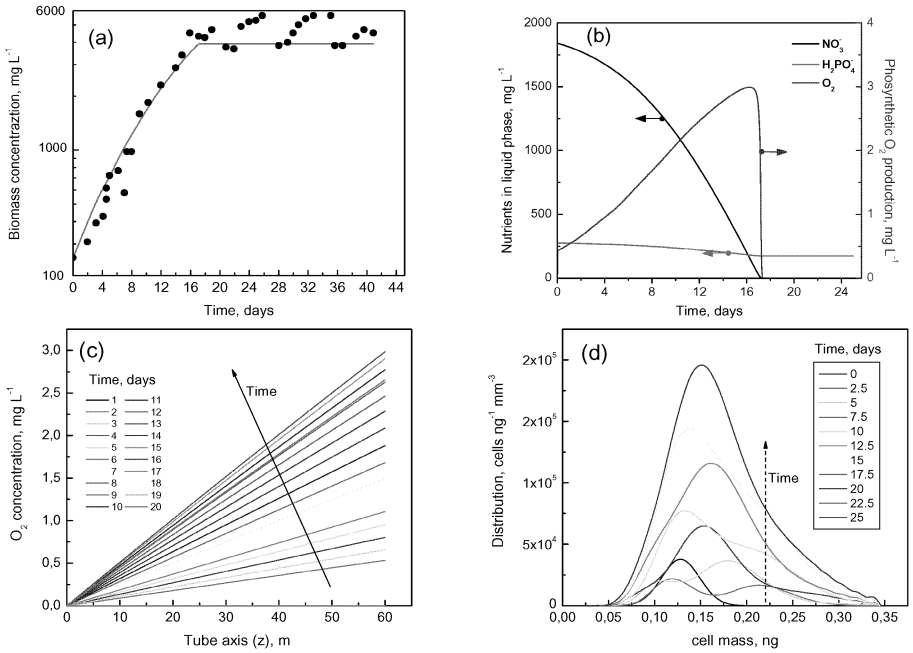

Figure 1. Model prediction for the biomass growth in the final section of the tube (a). Nutrients and oxygen concentrations in the final section of the tube (b). Oxygen concentration along the tube (c). Cell distribution in the final section of the tube (d).

While it is seen that the matching is quite good, thus demonstrating the validity of the proposed model, the latter one underestimates the experimental data when 17th days of culture is reached. This is because, once the stationary phase is reached during experiments, the photobioreactor was operated in a semi-continuous mode by stepwise replacement of its medium using suitable solutions (Travieso et al., 2001).

Since this situation is not accounted for in the present model, the matching with experimental data cannot be obtained in this part of the curve. Figure 1-b illustrates the calculated nutrient and oxygen concentrations as a function of time in the final section of the tube (z=L). From Figure 1-a and 1-b it is possible to observe that the stationary phase is reached when the total consumption of NO_3^- in the culture medium take place. Correspondingly, the photosynthetic activity is stopped, as demonstrated by the photosynthetic O_2 produced by algae which correspondingly drops to zero. Since the inhibitory action of O_2 plays a crucial role in the scaling-up of this technology, in Figure 2-a the axial profiles of O_2 concentration along the tube are reported for different times.
From figure 1-c it is possible to observe that the oxygen concentration within the liquid phase keeps on increasing inside the photobioreactors since the biomass, whose metabolism produces oxygen, constantly increases.
Finally, in Figure 1-d the time evolution of the cell mass distribution in the final section of the tube is reported. It is possible to observe that cell distribution displays a typical transient behaviour, thus moving back and forth as mitosis and growth take place. Starting from an unimodal population (with mode 0.128 ng), cell proliferation begins after that cells gain weight to reach their mitotic size which is close to the value of μ_0. At 2.5-3 days the distribution becomes bimodal with modes that correspond to peaks of mother and daughter cells. Then, the distribution once again becomes unimodal having an average cell mass different from the starting one. This behaviour, which may occur in real case, is well interpreted by the mass structured population balance proposed in the present and future work (Concas et al., 2009).

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