THE EFFECT OF RETROGRADE STIRRING OF SUSPENSION ON CO_2 BALANCE DURING MASS CULTIVATION OF ALGAE

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The effect of retrograde stirring of a suspension of autotrophic algae cultivated on an open cultivation platform on the fundamental engineering characteristics of CO_2 balance in the suspension is analyzed theoretically. Relationships for the actual concentration of CO_2 on the cultivation platform, for CO_2 losses due to desorption from the cultivation platform and for the degree of utilization of CO_2 supplied to the cultivation platform are derived. The retrograde stirring is shown to permit the use of longer cultivation platforms which is economically advantageous.

In one of the methods of mass cultivation of microscopic green algae described in the literature in some detail[1] the algal suspension flows down an inclined cultivation platform (at a 3% angle) and is locally stirred by suitably placed transverse partitions around which the suspension must flow. After leaving the cultivation platform the suspension is recycled to the platform through as absorber in which the suspension is supplied with carbon dioxide. A sufficient supply of CO_2 to the algal suspension is a major engineering problem because its concentration in the suspension decreases during suspension flow by its escape to the air and by its utilization by the algae. The desorbed CO_2 represents an economic loss because it cannot be re-utilized.

According to literature data[1] the concentration of CO_2 dissolved in a suspension of photosynthetic algae should not drop below 10 mg/l, corresponding to equilibrium with 0·7% CO_2 in the gaseous phase. On the other hand, the concentration of dissolved CO_2 should not exceed 66 mg/l, corresponding to equilibrium with 5% CO_2 in the gaseous phase. The range of CO_2 concentrations which may be considered as optimum for the algae may be even narrower (for *Scenedesmus quadricauda* the recommended range is 1·5–5% CO_2)[2]. As the algal suspension flows around the partitions of the cultivation platform, the arising turbulence prevents sedimentation of algal cells and brings about retrograde stirring of the suspension. The retrograde stirring will influence the concentration profile of CO_2 in the suspension on the cultivation platform and hence also CO_2 losses due to release to the atmosphere and the degree of utilization of CO_2 supplied to the suspension on the platform. Existing information[2,3] on the CO_2 balance in a flowing suspension on an open cultivation platform is based on the model of piston flow of suspension and the authors do not take the retrograde stirring into consideration. This is amended in the present communication.

Concentration Profile of CO_2 *in a Flowing Suspension*

Let us consider a unidirectional flow of suspension with retrograde stirring when suspension of layer thickness h flows along an inclined cultivation platform at a rate u. The length of the examined cultivation platform is L and it has a unit width. The differential balance of free CO_2 dissolved in the suspension in a steady state is expressed by:

$$u \frac{dC}{dx} - D \frac{d^2C}{dx^2} - r_1 + (YP + N)/h = 0\,, \tag{1}$$

where C is the concentration of free CO_2 dissolved in the suspension, D is the coefficient of longitudinal dispersion, x is the coordinate in the direction of suspension flow, r_1 is the rate of CO_2 increment due to chemical reaction, Y is a proportionality constant, P the rate of algal production referred to unit cultivation area, N is the mass flow of CO_2 by release from the suspension to the atmosphere. Since mass cultivation of algae in open cultivation platforms usually proceeds at pH values lower than 7 the effect of chemical reaction of CO_2 with OH^- ions on the concentration of CO_2 in the suspension may be neglected and only the hydration reaction may be considered:

$$CO_2 + H_2O \overset{k}{\rightleftharpoons} HCO_3^- + H^+\,, \tag{A}$$

where k is the rate constant. The decrement of CO_2 concentration in suspension caused by its desorption and by utilization by the algae can be partly compensated according to the reversible reaction (A) at the expense of HCO_3^- as chemical equilibrium is established during suspension flow. According to (A) the increase of CO_2 concentration is accompanied by a decrease of hydrogen ion concentration. One may expect that a pH change of the suspension caused by the chemical reaction (A) will be buffered by some components of the cultivation medium[4,5], such as phosphate and weak acid anions and by the algal cells themselves. A change of CO_2 concentration in the algal suspension thus does not bring about necessarily a pH change according to (A) such as would be found in an unbuffered system (pure water). Let us assume further that

$$r_1/r_2 = a\,, \tag{2}$$

where r_2 is the rate of decrease of hydrogen ions in the suspension caused by chemical reaction (A). The value of a will be greater than one because of the ability of the algal suspension to buffer pH changes.

The concentration of hydrogen ions in the suspension will generally change along the platform length. In the case of retrograde stirring of suspension the balance of these ions in an elementary unit of the suspension in a steady state is given by

$$u\,\frac{\mathrm{d}H}{\mathrm{d}x} - D\,\frac{\mathrm{d}^2H}{\mathrm{d}x^2} + r_2 = 0\,. \tag{3}$$

Combining Eq. (*1*), (*2*) and (*3*) we obtain

$$u\,\frac{\mathrm{d}C}{\mathrm{d}x} - D\,\frac{\mathrm{d}^2C}{\mathrm{d}x^2} + (YP + N)/h + \left(u\,\frac{\mathrm{d}H}{\mathrm{d}x} - D\,\frac{\mathrm{d}^2H}{\mathrm{d}x^2}\right)a = 0\,. \tag{4}$$

It follows from measuring the pH of an algal suspension along the length of its flow on the cultivation platform that the gradient $\mathrm{d}H/\mathrm{d}x$ for the given cultivation conditions (temperature, intensity of photosynthesis, flow hydrodynamics) is practically constant and hence the term $D(\mathrm{d}^2H/\mathrm{d}x^2)$ may be omitted from Eq. (*4*).

The following expression can be written for the mass flow of CO_2 by desorption from the suspension on the cultivation platform

$$N = K_L(C - C^+)\,, \tag{5}$$

where K_L is the mass transfer coefficient, C^+ the concentration of free CO_2 in the suspension at the interface between suspension and atmosphere. Since $C^+ \ll C$, Eq. (*5*) can be simplified to

$$N = K_LC\,. \tag{6}$$

By leaving out $D(\mathrm{d}^2H/\mathrm{d}x^2)$ from Eq. (*4*) and combining with Eq. (*6*) we obtain

$$u\,\frac{\mathrm{d}C}{\mathrm{d}x} - D\,\frac{\mathrm{d}^2C}{\mathrm{d}x^2} + (YP + K_LC)/h + (ua)\,.\,\mathrm{d}H/\mathrm{d}x = 0\,. \tag{7}$$

Introduction of dimensionless variables $z = x/L$, $\bar{C} = C/C_0$, where C_0 is the concentration of free CO_2 in suspension entering the cultivation platform, Eq. (*7*) becomes

$$(\mathrm{d}^2\bar{C}/\mathrm{d}z^2) - \mathrm{Bo}\,\mathrm{d}\bar{C}/\mathrm{d}z - \mathrm{Bo}\,K_LL\bar{C}/uh = (L/DC_0)\left[(YPL/h) + (ua)(\mathrm{d}H/\mathrm{d}z)\right], \tag{8}$$

where $\mathrm{Bo} = Lu/D$ is the Bodenstein number.

If the right-hand side of the equation does not depend on z, it has the general solution

$$\bar{C} = A\exp\left[(1 + \acute{a})(\mathrm{Bo}\,z/2)\right] + B\exp\left[(1 - a')(\mathrm{Bo}\,z/2)\right] - m/C_0\,, \tag{9}$$

where

$$a' = [1 + (4K_L L/uh\,\mathrm{Bo})]^{1/2}\,, \tag{9a}$$

$$m = YP/K_L + (auh/K_L)(\mathrm{d}H/\mathrm{d}x)\,. \tag{9b}$$

It can be shown that the second term of Eq. (*9b*) is much smaller than the first term and hence can be left out. Let us consider the following values of parameters of Eq. (*9b*): $u = 7\ \mathrm{cm\,s^{-1}}$, $h = 3{\cdot}8\ \mathrm{cm}$, $K_L = 6\,.\,10^{-3}\ \mathrm{cm\,s^{-1}}$ (ref.[3]), $a = 5$, $P = 1\ \mathrm{g\,m^{-2}\,.\,h^{-1}}$. To assess the magnitude of the gradient $\mathrm{d}H/\mathrm{d}x$ let us consider a drop of hydrogen ion concentration in the suspension amounting to $3\,.\,10^{-7}\ \mathrm{mol\,l^{-1}}$ over a flow distance of 30 m. Substituting the above values into Eq. (*9b*) we obtain $YP/K_L = 10^{-8}\ \mathrm{kg\,m^{-3}}$, $(auh/K_L)(\mathrm{d}H/\mathrm{d}x) = 2{\cdot}2\,.\,10^{-12}\ \mathrm{kg\,m^{-3}}$ and hence YP/K_L is much greater than the last term of Eq. (*9b*). In view of this fact we may write Eq. (*9b*) as

$$m = YP/K_L\,. \tag{9c}$$

The unknown constants A, B in Eq. (*9*) can be calculated from the limiting conditions:

$$\begin{aligned} z &= 0\,; \quad \bar{C} = 1 + \mathrm{Bo}^{-1}(\mathrm{d}\bar{C}/\mathrm{d}z)_0\,, \\ z &= 1\,; \quad \mathrm{d}\bar{C}/\mathrm{d}z = 0\,. \end{aligned} \tag{10}$$

From Eq. (*9*) and the limiting conditions (*10*) and taking into account Eq. (*9c*) the course of dimensionless concentration of CO_2 in suspension is expressed by

$$\begin{aligned} \bar{C} = {} & 2[1 + (YP/K_L C_0)]\,.\,\{(1 + a')\exp[(\mathrm{Bo}\,.\,a'/2) + (\mathrm{Bo}\,.\,z/2)(1 - a')] - \\ & - (1 - a')\exp[(-\mathrm{Bo}\,.\,a'/2) + (\mathrm{Bo}\,.\,z/2)(1 + a')]\}\,.\,[(1 + a')^2\exp(\mathrm{Bo}\,.\,a'/2) - \\ & - (1 - a')^2\exp(-\mathrm{Bo}\,.\,a'/2)]^{-1} - YP/K_L C_0\,. \end{aligned} \tag{11}$$

From the engineering point of view the important quantity is the concentration of CO_2 at the exit of suspension from the cultivation platform since it must be maintained at an optimum level when the photosynthesis of algal cells is not limited by the availability of CO_2 and when no excessive losses of CO_2 are incurred due to desorption from the cultivation platform. The dimensionless CO_2 concentration in an algal suspension at the exit from the cultivation platform ($z = 1$) is expressed with the aid of Eq. (*11*) as follows:

$$\begin{aligned} \bar{C}_L = {} & \{4a'[1 + (YP/K_L C_0)]\exp(\mathrm{Bo}/2)\}\,[(1 + a')^2\exp(\mathrm{Bo}\,.\,a'/2) - \\ & - (1 - a')^2\exp(-\mathrm{Bo}\,.\,a'/2)]^{-1} - YP/K_L C_0\,. \end{aligned} \tag{12}$$

For $YP/K_LC_0 = 0$ the equation reduces to the analogous expression derived by Levenspiel[6] for the case of unidirectional flow of a retrogradely mixed liquid through a tube plus a first-order chemical reaction taking place in the liquid[7]. Instead of the first-order rate constant, however, we have here the expression K_L/h.

For a situation resembling piston flow of suspension as may prevail on a platform of sufficient length the value of $(1 - a')^2 \exp(-\text{Bo} \,.\, a'/2)$ in Eq. (*12*) will be substantially smaller than $(1 + a')^2 \exp(\text{Bo} \,.\, a'/2)$. Eq. (*12*) then reduces to

$$\bar{C}_L = [4a'/(1 + a')^2]\,[1 + (YP/K_LC_0)] \,.\, \exp[-\text{Bo}(a' - 1)/2] - YP/K_LC_0 \,. \quad (13)$$

For a desired concentration C_L at the exit of suspension from the cultivation platform one must maintain the concentration of CO_2 in the suspension entering the cultivation platform at a value given by

$$C_0 = [C_L + (YP/K_L)]\,[(1 + a')^2/4a'] \,.\, \exp[(\text{Bo}/2)(a' - 1)] - YP/K_L \,, \quad (14)$$

as follows from Eq. (*13*).

Eq. (*14*) indicates that C_0 will depend among other things on the Bodenstein number which characterizes the intensity of retrograde stirring. In the limiting case of piston flow ($\text{Bo} = \infty$) equations (*14*) and (*9a*) yield

$$C_{0p} = [(YP/K_L) + C_L] \exp(K_LL/uh) - YP/K_L \,. \quad (15)$$

This equation is formally identical with the expression reported by Smutek and coworkers[2]. A similar expression was published by the present author[3] under the assumption that the suspension pH during its flow along the cultivation platform is constant. This assumption is not fully met according to observed data (on a 30 m platform the pH rose by 0·1–0·3 units as the suspension flowed down the platform).

The effect of the Bodenstein number on the entering concentration of CO_2 in the suspension may be assessed for given values of YP/K_L and C_L from the expression derived from Eq. (*14*):

$$C' = [C_0 + (YP/K_L)]/[C_L + (YP/K_L)] = [(1 + a')^2/4a'] \,.\, \exp[\text{Bo}(a' - 1)/2] \,. \quad (16)$$

The dependence is depicted in Fig. 1, showing that an increase of retrograde stirring intensity (decrease of Bo) brings about a decrease of C', *i.e.* a decrease of C_0 in Eq. (*16*). Retrograde stirring of a suspension on the cultivation platform thus makes it possible to saturate the algal suspension entering the cultivation area to lower levels of CO_2 concentration which is advantageous in view of decreasing the losses of CO_2 by desorption into free atmosphere as the suspension flows along the platform.

Losses of CO_2 by Desorption from the Cultivation Platform

An algal suspension on the cultivation platform must be supplied in a steady state with such an amount of CO_2 as to compensate for losses of CO_2 due to desorption and utilization by algae, hence

$$Q = R + YPL, \tag{17}$$

where Q is the mass flow of CO_2 dissolved in the suspension entering the cultivation platform, R is the mass flow of CO_2 by desorption from the cultivation platform. Both Q and R refer to a platform of length L and of unit width. Using dimensionless CO_2 concentration one can write for R

$$R = K_L C_0 L \int_0^1 \bar{C} \,.\, \mathrm{d}z \,. \tag{18}$$

To solve the integral one must know the dependence of $\bar{C}$ on z. In the case that the character of suspension flow will resemble piston flow one can neglect in the denominator of Eq. (*11*) the $(1 - a')^2$ term in comparison with the $(1 + a')^2$ term without incurring any considerable error. Eq. (*11*) then assumes the form:

$$\begin{aligned}\bar{C} = {} & 2[1 + YP/K_L C_0)] \{(1 + a') \exp [(\mathrm{Bo} \,.\, a'/2) + (\mathrm{Bo} \,.\, z/2)(1 - a')] - \\ & - (1 - a') \exp [(-\mathrm{Bo} \,.\, a'/2) + (\mathrm{Bo} \,.\, z/2)(1 + a')]\} \,. \\ & . [(1 + a')^2 \exp (\mathrm{Bo} \,.\, a'/2)]^{-1} - YP/K_L C_0 \,. \end{aligned} \tag{19}$$

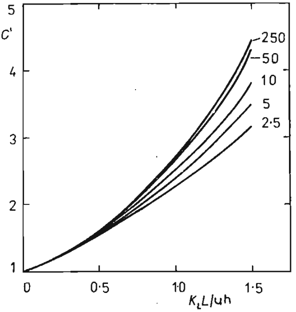

FIG. 1

Dependence According to Eq. (*16*) for Different Values of the Bodenstein Number (Bo = uL/D)

Substituting for $\bar{C}$ from Eq. (*19*) into Eq. (*18*) and integrating we obtain

$$R = 4K_L L[C_0 + (YP/K_L)] \{[\exp(\text{Bo}/2)(1 - a')] - 1\} \,.\, \text{Bo}^{-1}[1 - (a')^2]^{-1} - YPL. \qquad (20)$$

Substituting for C_0 from Eq. (*14*) into Eq. (*20*) we obtain

$$R = [C_L + (YP/K_L)](1 + a')\{[\exp(\text{Bo}/2)(a' - 1)] - 1\} K_L L(\text{Bo} \,.\, a')^{-1} \,.\, (a' - 1)^{-1} - YPL; \qquad (21)$$

For the limiting case of piston flow of suspension (Bo = ∞) Eq. (*21*) becomes

$$R_p = uh[C_L + (YP/K_L)] \{\exp(K_L L/uh)] - 1\} - YPL. \qquad (22)$$

With piston flow the losses of CO_2 due to desorption will be maximal and they will decrease with increasing intensity of retrograde stirring of the suspension (decreasing Bo). This is best visualized by transforming Eq. (*21*) to

$$R' = (R + YPL)/(R_{\min} + YPL) = (1 + a')\{[\exp(\text{Bo}/2)(a' - 1)] - 1\} \,.\, [\text{Bo} \,.\, a'(a' - 1)]^{-1}, \qquad (23)$$

where $R_{\min} = K_L L C_L$ is the value of R at the exit of suspension from the platform where the concentration of dissolved CO_2 in suspension attains minimum values of C_L. The dependence described by Eq. (*23*) is depicted in Fig. 2, showing that an increaase of retrograde stirring (decrease of Bo) brings about a decrease of R' and hence of R, as required by Eq. (*23*). Retrograde stirring of the suspension on the cultivation platform is thus advantageous from the point of view of CO_2 losses by desorption.

Degree of Utilization of CO_2 *Supplied to the Cultivation Platform*

The degree of utilization may be described as[3]

$$\varphi = YPL/(R + YPL)\,. \qquad (24)$$

This relationship describes the ratio between utilized CO_2 and CO_2 supplied to the platform. The ratio is always less than one because of desorption losses. Substituting for R from Eq. (*21*) into Eq. (*24*) we obtain

$$\varphi/\phi = [\text{Bo} \,.\, a'(a' - 1)/(1 + a')] \{[\exp(\text{Bo}/2)(a' - 1)] - 1\}^{-1}, \qquad (25)$$

where

$$\hat{\varphi} = 1/[1 + (K_L C_L / YP)] \tag{26}$$

is the maximum value corresponding to the case that the CO_2 concentration over the entire platform area is the same as that in the exit. The dependence given by Eq. (*25*) is depicted in Fig. 3, showing that an increase of intensity of retrograde stirring (decrease of Bo) brings about an increase of $\varphi/\hat{\varphi}$. Utilization of CO_2 by the platform with retrograde stirring will thus be better than in a the case of piston flow of suspension.

For a quantitative estimation of the value of the Bodenstein number in an atypical system such as the flow of suspension around transverse partitions on a cultivation platform no reliable data are available. It can be assumed, however, that retrograde stirring on such a cultivation platform will be much more intense than during turbulent flow of a liquid through a smooth pipe. For turbulent flow through a pipe of length L and inner diameter d: the Bodenstein number may be assessed from relationship[8]: $\mathrm{Bo} = uL/d = 0{\cdot}33\ (L/d)$. For a cultivation platform 30 m long and suspension layer thickness 4 cm ($= d$) the above relation yields Bo = 250. This may be taken as the upper limit for the Bo number in the present case.

From the engineering point of view it is necessary to know the length of the platform to assess its efficiency. An example of calculating the required platform length is given below.

Let us consider an algal suspension flowing over a cultivation platform at a rate of $u = 7\ \mathrm{cm\,.\,s^{-1}}$, the thickness of the suspension layer is $h = 5$ cm. Let us assume a maximum rate of algae production $P = 5\ \mathrm{g\,m^{-2}\,h^{-1}}$; $Y = 2{\cdot}17$ g CO_2 per g of algae[9]. For the mass transfer coefficient of CO_2 desorption from the suspension to the atmosphere let us take $K_L = 10^{-2}\ \mathrm{cm\,s^{-1}}$ (ref.[10]). The CO_2 concentration in the suspension entering the cultivation platform is $C_0 = 66\ \mathrm{mg\,l^{-1}}$,

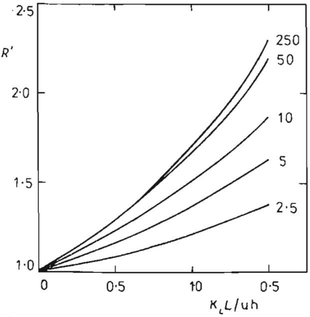

FIG. 2

Dependence According to Eq. (*23*) for Different Values of Bo

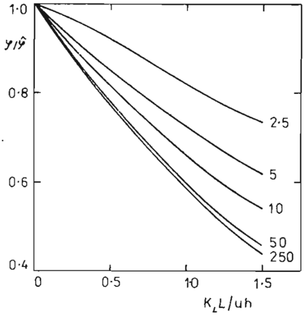

FIG. 3

Dependence According to Eq. (*25*) for Different Values of Bo at the exit it is $C_L = 10 \text{ mg l}^{-1}$. Substitution of these values into Eq. (*16*) yields: $C' = [C_0 + (YP/K_L)]/[C_L + (YP/K_L)] = 2{\cdot}4$. For $C' = 2{\cdot}4$ Fig. 1 yields for given Bo numbers (250, 50, 10, 5, 2·5) the following values of $K_L L/uh$: 0·875, 0·887, 0·937, 1·000, 1·075. Substitution for K_L, u, h into $K_L L/uh$ yields the following values of L (corresponding to the various Bo numbers above): 43·7 m, 44·4 m, 46·8 m, 50, 53·7 m. By increasing the intensity of retrograde stirring of suspension one can thus increse the length of the cultivation platform, in the given range by 10 m. From the engineering point of view it may be stated that the cultivation platform is the more economical the longer it is[2]. For this reason it is advisable to employ such cultivation platforms where the flow of suspension would be accompanied by a high degree of retrograde stirring.

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