

THE MASS TRANSFER COEFFICIENT FOR CO₂ DESORPTION FROM A TURBULENT FLOW OF AN ALGAL SUSPENSION

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On the basis of the penetration theory an expression for the mass transfer coefficient for CO₂ desorption from a turbulent algal suspension into free atmosphere is derived. The predictions of the expression are compared with experimental results.

Much attention has been recently focussed on mass cultivation of green microscopic algae which find a variety of uses. In one of the types of mass cultivation the algal suspension flows along an inclined cultivation platform (at a 3% angle) placed in the open air. The thickness of the suspension layer is several cm and its mixing is ensured with the aid of transverse partitions around which the suspension flows. Turbulence in the suspension sets in which prevents the cells from sedimenting. A more detailed description of the cultivation platform and some fundamental aspects of the cultivation are mentioned by Šetlík and coworkers¹.

Carbon dioxide is usually supplied to an algal suspension by absorption at a suitable place of the recycling system. During suspension flow along a cultivation platform several tens m long much of the CO₂ is lost due to desorption into the atmosphere. As shown by drawing a balance sheet for CO₂ (ref.^{2,3}) one of the basic parameters affecting the utilization of CO₂ supplied to the cultivation platform is the mass transfer coefficient for CO₂ desorption. In the present communication we intend to analyze theoretically the desorption of CO₂ from the point of view of the penetration theory of mass transfer, taking into account the uptake of CO₂ by photosynthetic algae and the chemical reactivity of CO₂ in the suspension.

THEORETICAL

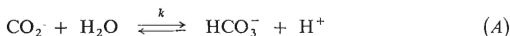
According to the penetration theory of mass transfer liquid vortices are transported from the turbulent core to the liquid-gas interface where they remain for time t_e during which the interface mass transfer takes place. Then they migrate back to the liquid and are replaced by other vortices from the liquid core. In the present case an unstable desorption of CO₂ from the suspension elements will proceed to the free

atmosphere. In a suspension element algal photosynthesis will take place simultaneously, during which suspension-dissolved CO_2 is utilized. The decrement of CO_2 will be partly compensated by its release from chemically bound forms in the suspension (bicarbonate ions). An unstable diffusion of CO_2 taking place in a suspension element toward the interface will be described by:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + r_1 - r_2, \quad (1)$$

where C is the concentration of free CO_2 in the suspension, r_1 is the rate of CO_2 increase due to chemical reaction, r_2 is the rate of CO_2 uptake by photosynthesizing algae, D is the diffusivity of CO_2 in the suspension, x is the distance from the suspension-gas interface.

Algae are usually cultivated on open-air platforms at a neutral pH when the CO_2 dissolved in the suspension participates in the reversible chemical reaction:



where k is a rate constant. For r_1 of Eq. (A) we obtain thus:

$$r_1 = k(C - C_e) \quad (2)$$

where the equilibrium concentration of dissolved CO_2 is given by

$$C_e = HB/K_1. \quad (3)$$

In this expression H and B represent concentrations of hydrogen and bicarbonate ions in the suspension, respectively, K_1 is the equilibrium constant of reaction (A).

In deriving the expression for r_2 let us assume that the uptake of CO_2 by the algae is proportional to the rate of photosynthesis r_p (proportionality coefficient Y) per unit suspension volume.

$$r_2 = Yr_p. \quad (4)$$

The simplest mechanism of photosynthesis as suggested by Lumry and Rieske⁴ yields according to Fredrickson and coworkers⁵ the following expression for r_p :

$$r_p = k'_D T^+, \quad (5)$$

where k'_D is the rate constant of photosynthetic reactions taking place in the dark,

T^+ is the concentration of excited centres in the algal suspension. (These centres may be represented by clusters of molecules of a pigment or an enzyme which absorb light energy bringing about excitation). From the Lumry-Rieske mechanism of photosynthesis the following differential equation for T^+ may be derived⁵:

$$\frac{dT^+}{dt} = k'_L I (T_0 - T^+) - k'_D T^+ \quad (6)$$

In this expression t is time, k'_L is the rate constant of photosynthetic reactions taking place in the light of intensity I , T_0 is the concentration of active centres (excited and nonexcited) in the algal suspension.

In suspension elements that have penetrated from the turbulent core to the suspension-atmosphere interface the light intensity is I_0 with which the suspension is being illuminated. After integration for $I = I_0$, Eq. (5) and (6) yield

$$r_p = (k'_L k'_D T_0 I_0) / (k'_L I_0 + k'_D) + k'_D \{ T_0^+ - [(k'_L T_0 I_0) / (k'_L I_0 + k'_D)] \} \cdot \exp [-(k'_L I_0 + k'_D) t], \quad (7)$$

where T_0^+ is the value of T^+ at time zero during which an element from the suspension core penetrates to the suspension-free atmosphere interface. T_0^+ thus corresponds to the conditions obtained in the suspension core.

For a steady state ($t \rightarrow \infty$) we obtain from Eq. (7)

$$r_p = \hat{r}_p I_0 / [I_0 + (k'_D / k'_L)] \quad (8)$$

where $\hat{r}_p = k'_D T_0$ is the maximum rate of photosynthesis when all the active centres will be excited. According to Eq. (8) the dependence of the rate of photosynthesis on light intensity will be hyperbolic. Eq. (8) has the same formal structure as the Michaelis-Menten equation (*e.g.*, Aiba and coworkers⁶) used in enzyme kinetics of microbial growth with a single limiting substrate. The light intensity is thus in our case a special type of substrate for photosynthesizing algae.

Using Eq. (8), Eq. (7) can be transcribed:

$$r_p = \hat{r}_p I_0 / [I_0 + (k'_D / k'_L)] + \{ r_{pT} - (\hat{r}_p I_0) / [I_0 + (k'_D / k'_L)] \} \cdot \exp [-(k'_L I_0 + k'_D) t] \quad (9)$$

where $r_{pT} = k'_D T_0^+$ is the rate of photosynthesis under the conditions of the turbulent core of the suspension.

Substitution from Eq. (2), (4) and (9) into Eq. (1) then yields

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + k(C_e - C) - Y\hat{r}_p I_0 / (I_0 + K_1) - Y[r_{pT} - (\hat{r}_p I_0) / (I_0 + K_1)] \cdot \exp[-(k'_L I_0 + k'_D) t], \quad (10)$$

where

$$K_1 = k'_D / k'_L. \quad (10a)$$

During the time of contact t_e of a suspension element with free atmosphere the amount of desorbed CO_2 from a unit surface area of an element is given by:

$$N = \int_0^{t_e} D \left. \frac{\partial C}{\partial x} \right|_{x=0} dt. \quad (11)$$

Solution of (10) for initial and limiting conditions:

$$C = C^0, \quad x > 0, \quad t = 0, \quad C = C_r, \quad x = 0, \quad t > 0 \quad (12)$$

and substitution of $\partial C / \partial x$ into (11) yields (see the Appendix):

$$N = -C_r [(D/k)^{1/2} \cdot (\frac{1}{2} + kt_e) \cdot \text{erf} \sqrt{(kt_e)} + (Dt_e/\pi)^{1/2} \cdot \exp(-kt_e)] + C^0 (D/k)^{1/2} \cdot \text{erf} \sqrt{(kt_e)} - (a_1 \sqrt{D/k^3}) [(kt_e - \frac{1}{2}) \cdot \text{erf} \sqrt{(kt_e)} + (kt_e/\pi)^{1/2} \cdot \exp(-kt_e)] - (D/k)^{1/2} (a_2/a_3) \cdot \text{erf} \sqrt{(kt_e)} + [D/(k - a_3)]^{1/2} \cdot (a_2/a_3) [\exp(-a_3 t_e)] \cdot \text{erf} [(k - a_3) t_e]^{1/2}; \quad (13)$$

where a_1, a_2, a_3 depend among other things on the rate constants of photosynthesis k'_D, k'_L (Eqs. 30–32 in the Appendix).

To estimate the value of k'_D and k'_L Fredrickson and coworkers⁵ use experimental data (Tamiya and coworkers⁷) on the growth of *Chlorella ellipsoidea* at 25°C. On the assumption that 1 litre algal cells release during photosynthesis some 14 mol oxygen, Fredrickson's data give: $k'_D = 3.54 \text{ d}^{-1}$, $k'_L = 1.19 \text{ d}^{-1} \text{ klx}^{-1}$. Taking further the maximum intensity of light incident on the suspension on the cultivation platform to be $I_0 = 100 \text{ klx}$, Eq. (32) yields $a_3 = 1.42 \cdot 10^{-3} \text{ s}^{-1}$. Since the rate constant k of chemical reaction (A) attains values of roughly 10^{-2} s^{-1} (e.g. Pinsent and coworkers⁸) the value of a_3 may be neglected with respect to k whereupon Eq. (13) simplifies to:

$$N = \{C^0 - C_r(\frac{1}{2} + kt_e) - (a_1/k)(kt_e - \frac{1}{2}) - (a_2/a_3)[1 - \exp(-a_3 t_e)]\} \cdot (D/k)^{1/2} \cdot \text{erf} \sqrt{(kt_e)} - [C_r + (a_1/k)] (Dt_e/\pi)^{1/2} \cdot \exp(-kt_e). \quad (14)$$

The mass transfer coefficient for CO₂ desorption may be defined as

$$K = N / (C^0 - C_r) t_e \quad (15)$$

Eq. (14) and (15) combine to

$$K = (D/k)^{1/2} [(C^0 - C_r) t_e]^{-1} \{ C^0 - C_r (\frac{1}{2} + kt_e) - (a_1/k) (kt_e - \frac{1}{2}) - \\ - (a_2/a_3) [1 - \exp(-a_3 t_e)] \} \cdot \operatorname{erf} \sqrt{(kt_e)} - [(C^0 - C_r) t_e]^{-1} \cdot \\ \cdot [C_r + (a_1/k)] \cdot (Dt_e/\pi)^{1/2} \cdot \exp(-kt_e); \quad (16)$$

For sufficiently small values of kt_e it holds that

$$\operatorname{erf}(kt_e)^{1/2} = 2(kt_e/\pi)^{1/2}, \exp(-kt_e) = 1 - kt_e \quad (17)$$

Eq. (16) thus reduces to

$$K = 2(C^0 - C_r)^{-1} (Dt_e/\pi)^{1/2} \{ [(C^0 - C_r)/t_e] - (a_2/2a_3 t_e) [1 - \exp(-a_3 t_e)] - \\ - [C_r + (a_1/k)] \cdot (k/2) \} \quad (18)$$

Since a_3 attains values of about 10^{-3} s^{-1} , for short periods of contact t_e it will hold that $a_3 t_e \ll 1$ and Eq. (18) can be reduced further to

$$K = 2(C^0 - C_r)^{-1} (Dt_e/\pi)^{1/2} \{ [(C^0 - C_r)/t_e] - (a_2/2) - [C_r + (a_1/k)] \cdot (k/2) \} \quad (19)$$

On substitution for a_1 , a_2 and a_3 from Eq. (30)–(32) we obtain from (19):

$$K = 2(C^0 - C_r)^{-1} (Dt_e/\pi)^{1/2} \{ [(C^0 - C_r)/t_e] + (C_e - C_r) (k/2) - (Y\hat{p}_p/2) \} \quad (20)$$

For the case that carbon dioxide dissolved in the algal suspension is in chemical equilibrium ($C^0 = C_e$) and on the assumption that the concentration of free CO₂ in the suspension core is much greater than the concentration of CO₂ in the suspension-atmosphere interface ($C^0 \gg C_r$), Eq. (20) yields:

$$K = 2(Dt_e/\pi)^{1/2} \left[\frac{1}{t_e} + \frac{k}{2} - (Y\hat{p}_p/2C_e) \right] \quad (21)$$

In the case that the effect of a chemical reaction (A) and of algal photosynthesis on

the mass transfer coefficient is insignificant, Eq. (21) yields the well-known relationship:

$$K^+ = 2(D/\pi t_c)^{1/2}. \quad (22)$$

The ratio of mass transfer coefficients from Eq. (21) and (22) is given by:

$$K/K^+ = 1 + [k - (Y\hat{r}_p/C_e)] (t_c/2). \quad (23)$$

DISCUSSION

Let us estimate the magnitude of $[k - (Y\hat{r}_p/C_e)]$. According to literature data⁸ the rate constant k may attain values of $4 \cdot 10^{-2} \text{ s}^{-1}$ at 30°C. If the maximum rate of algal production per unit cultivation area is $5 \text{ g m}^{-2} \text{ h}^{-1}$ and the suspension thickness is 5 cm, then $\hat{r}_p = 2.78 \cdot 10^{-8} \text{ g cm}^{-3} \text{ s}^{-1}$. If the minimum admissible concentration of CO_2 in suspension is 10^{-5} g/cm^3 (ref.²) and $Y = 2.17 \text{ g CO}_2$ per g algae (Simmer⁹) we obtain $Y\hat{r}_p/C_e = 6 \cdot 10^{-3} \text{ s}^{-1}$, i.e. a value about one order of magnitude lower than k . In expression (23) one can thus with a fair approximation neglect the $Y\hat{r}_p/C_e$ term so that K/K^+ is practically unaffected by algal photosynthesis. This result is in agreement with the finding of Yagi and Yoshida¹⁰ that the oxygen transfer coefficient during its absorption from the air by a mixed culture of aerobic microorganisms is practically unaffected by microbial respiration. Eq. (23) may then be written as:

$$K/K^+ = 1 + (kt_c/2). \quad (24)$$

For $k \leq 0.1 \text{ s}^{-1}$ which may obtain in our case the effect of the chemical reaction of the transferred component on the transfer coefficient may be neglected¹¹. From Eq. (24) we then obtain $K/K^+ = 1$. This result was confirmed by experimental data from which it follows that the mass transfer coefficients for CO_2 absorption by a turbulent flow of algal suspension, water and nutrient medium are practically identical for a given Reynolds number of the liquid¹².

Let us further assume that the mass transfer coefficient for CO_2 desorption from an algal suspension into the atmosphere can be calculated from the dimensionless relationship:

$$\text{Sh} = a \text{Re}^{7/8} \text{Sc}^{1/2}, \quad (25)$$

where $\text{Sh} = K^+H/D$; a is the proportionality factor, $\text{Re} = vH/\nu$, $\text{Sc} = \nu/D$. In these expressions H is the thickness of the suspension layer, ν velocity v its kinematic viscosity of suspension. Eq. (25) is formally identical with the expression for mass transfer

from the pipe wall into turbulent flow of a liquid¹³, the only difference being that instead of the pipe diameter we take here the layer thickness as a characteristic geometrical dimension.

If we substitute for v in the Reynolds number according to Manning's expression for flow through an open channel¹⁴

$$v = (1/n) H^{2/3} S^{1/2}, \quad (26)$$

where n is the roughness coefficient, $S = \sin \alpha \sim \text{tg } \alpha$ (α being the inclination of the channel bottom) Eq. (25) yields

$$K^+ = a' v^{11/16} \quad (27)$$

where

$$a' = aD^{1/2} S^{3/32} / v^{3/8} n^{3/16}. \quad (27a)$$

For a given geometry of the system this depends solely on the physical properties of the liquid.

Fig. 1 shows the values of the mass transfer coefficient observed from experimental data of CO₂ absorption by a flowing turbulent layer of a suspension of *Scenedesmus quadricauda* grown at 30°C on a model of cultivation platform¹², plotted against the observed mean rate of flow v of the suspension. Fig. 1 confirms satisfactorily the predicted relationship (27).

The mass transfer coefficient for CO₂ desorption from an algal suspension during their mass cultivation on an open cultivation platform can thus be calculated from relationship (25) provided that the rate of flow of suspension on the cultivation platform obeys Manning's equation (26).

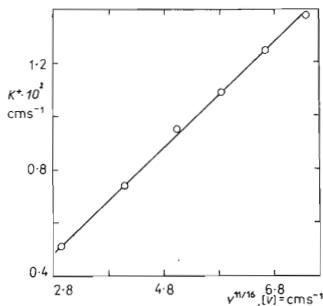


FIG. 1

Experimentally Established Dependence of the Mass Transfer Coefficient for CO₂ on the Rate of Suspension Flow along the Cultivation Platform

APPENDIX

Derivation of Eq. (13): On the assumption of constant C_e a Laplace transform of Eq. (10) yields

$$\begin{aligned} \bar{C} = & A \cdot \exp [x(p+k)^{1/2}/D^{1/2}] + B \cdot \exp [-x(p+k)^{1/2}/D^{1/2}] - \\ & - [Yr_p I_0 (I_0 + K_1)^{-1} - kC_e] / [p(p+k)] - Y[r_{pT} - \hat{r}_p I_0 (I_0 + K_1)^{-1}] / \\ & / [(p+k'_L I_0 + k'_D)(p+k)] + C^0 / (p+k); \end{aligned} \quad (28)$$

where C^0 is the value of C at time zero, p is the Laplacean parameter; A, B are undefined constants, $K_1 = k'_D/k'_L$.

For $A = 0$ and the limiting condition $x = 0, C = C_r$ and for $t > 0$ Eq. (1) yields:

$$\begin{aligned} \bar{C} = & \{ (C_r/p) - [C^0/(p+k)] + [a_1/p(p+k)] + [a_2/(p+a_3)(p+k)] \} \cdot \\ & \cdot \exp [-x(p+k)^{1/2}/D^{1/2}] - [a_1/p(p+k)] - [a_2/(p+a_3)(p+k)] + \\ & + C^0/(p+k), \end{aligned} \quad (29)$$

where

$$a_1 = [Yr_p I_0 / (I_0 + K_1)] - kC_e, \quad (30)$$

$$a_2 = Y[r_{pT} - \hat{r}_p I_0 (I_0 + K_1)^{-1}], \quad (31)$$

$$a_3 = k'_L I_0 + k'_D. \quad (32)$$

For a Laplacean transform of Eq. (11) it holds that¹⁵:

$$\bar{N} = \frac{1}{p} \cdot D \frac{\partial \bar{C}}{\partial x} \Big|_{x=0}. \quad (33)$$

Eq. (29) and (33) yield further:

$$\begin{aligned} \bar{N} = & -(1/p) \{ (C_r/p) - [C^0/(p+k)] + [a_1/p(p+k)] + [a_2/(p+a_3)(p+k)] \} \cdot \\ & \cdot [(p+k)D]^{1/2}. \end{aligned} \quad (34)$$

A reverse transform of this equation¹⁶ and rearrangement yields Eq. (13).

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