

Original Research Article

Relation between injection and transfer of CO₂ and the pH of the medium

ABSTRACT

Of all the photosynthetic organisms, microalgae are the biggest users of CO₂ and can fix large amounts of this compound. In algal biomass production systems, the requirement of carbon is usually supplied through CO₂, continuously or intermittently. The relative concentrations of inorganic carbon species determine the pH and, in turn, are determined by the pH of the medium. This study aimed to establish a relation between the variation in CO₂ concentration and the pH of the medium and validate the equation proposed for the transfer of CO₂ during the supply of this gas in the liquid medium in a carbon dioxide biofixation process in an open raceway type bioreactor, provided with a carbon dioxide injection system. The experiments were conducted in a 200 L open raceway type bioreactor, in which a gas injection system was employed where air enriched with 12% of the medium at a specific flow rate of 0.05 min⁻¹. An equation was established to determine the pH variation from the variation of the concentration of CO₂ in the environment. The data obtained from the proposed equation were satisfactorily explained by experimental data ($r^2 = 0.90$).

Key words: CO₂, supply, pH, microalgae

INTRODUCTION

The photoautotrophic growth of microalgae requires the supply of CO₂ as a carbon source. At the same time, the supply of CO₂ helps to control the pH of the culture. Chemical analyses show that microalgal biomass contains

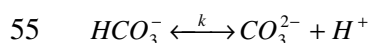
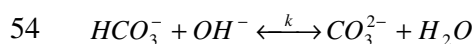
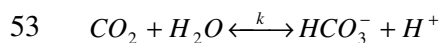
29 40 to 50% of carbon, which suggests that approximately 1.5 to 2.0 kg of
30 carbon dioxide is needed to produce 1.0 kg of biomass [9].

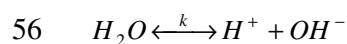
31 The transfer of CO₂ into the culture medium is a factor that has been
32 gaining attention in studies in chemical and biochemical engineering. Theories
33 and experimental correlations have been well developed. However, they only
34 provide approximate and/or relative estimates of transfer rates. In the final
35 analysis, these rates must be empirically determined from prototypes and
36 pilots. This is especially true for the carbonation of open ponds, where
37 instances of irregular surfaces are frequent due to turbulence, wind and
38 bubbles. These disturbances may cause a significant effect on gas transfer in
39 tanks [1].

40 The generally used explanation for the mechanism of gas transfer is
41 the dual-film theory. According to this theory, there are two films, a liquid and
42 a gas, the gas-liquid interface which promotes most of the resistance against
43 the passage of gas molecules within the gas phase to the liquid phase. For
44 high solubility gases in the liquid phase, for example, absorption of SO₂ in
45 water, the main absorption resistance is that offered by the gas film. For low
46 solubility gases in the liquid phase, for example, absorption of oxygen and
47 CO₂ in aqueous solutions, the resistance is limited by the liquid film. For
48 intermediate solubility gases, both films can offer significant resistance [6].

49 The predominant chemical reactions in the culture medium used to
50 obtain microalgal biomass are presented below:

51





57 The relationship between the chemical species of inorganic carbon and
58 pH of the medium may be expressed by the dissociation constants K_1 and K_2 ,
59 shown in Equations 5.2.1 and 5.2.2.

$$60 \quad K_1 = \frac{H^+ \cdot HCO_3^-}{H_2CO_3^*} \quad \text{Equation 5.2.1}$$

$$61 \quad K_2 = \frac{H^+ \cdot CO_3^{2-}}{HCO_3^-} \quad \text{Equation 5.2.2}$$

62 Where, according to Carmouze (1994) [2]:

$$63 \quad K_1 = 4,4361 \times 10^{-7}$$

$$64 \quad K_2 = 4,6881 \times 10^{-11}$$

$$65 \quad \alpha_0 = \frac{1}{\left(1 + \left(\frac{K_1}{H^+}\right) + \frac{K_1 K_2}{H^{+2}}\right)} \quad \text{Equation 5.2.3}$$

$$66 \quad \alpha_1 = \frac{1}{\left(1 + \left(\frac{H^+}{K_1}\right) + \frac{K_2}{H^+}\right)} \quad \text{Equation 5.2.4}$$

$$67 \quad \alpha_2 = \frac{1}{\left(1 + \left(\frac{H^{+2}}{K_1 K_2}\right) + \frac{H^+}{K_2}\right)} \quad \text{Equation 5.2.5}$$

$$68 \quad CO_2 = \alpha_0 * CT \quad \text{Equation 5.2.6}$$

$$69 \quad HCO_3^- = \alpha_1 * CT \quad \text{Equation 5.2.7}$$

$$70 \quad CO_3^{2-} = \alpha_2 * CT \quad \text{Equation 5.2.8}$$

71 Where CT_t is the total concentration of inorganic carbon in the medium (H_2CO_3, CO_3^{2-} e CO_2) HCO_3^-

73 Production of OH^- occurs in the conversion of both bicarbonate as well
74 as carbonate to CO_2 , increasing the medium pH. For this reason, in an
75 intensive cultivation of microalgae, it is not possible to achieve complete
76 consumption of the substrate present in the medium without pH correction,
77 since the same reaches values close to 14, inhibiting the growth of microalgae
78 [7].

79 This study aimed to establish a relation between the change in CO_2
80 concentration and the pH of the medium and validate the proposed equation
81 for the transfer of CO_2 during the supply of this gas in the liquid medium in a
82 process of carbon dioxide biofixation in an open raceway bioreactor, provided
83 with a carbon dioxide injection system.

84 MATERIALS AND METHODS

85 CO_2 supply system

86 The determinations of the global transfer coefficient of CO_2 (k_{LaCO_2})
87 were held in open raceway bioreactor (2.50 x 0.70 x 0.40 m), with a volume of
88 200 L, in which a gas injection system was employed (Figure 5.2.1) where
89 enriched air with 12% CO_2 was injected into the medium at a specific flow rate
90 of 0.05 min^{-1} . This system was used to provide a homogeneous distribution of
91 the mass of gas being transferred to the liquid medium via a pipe provided
92 with nozzles of a sintered material along the photobioreactor.

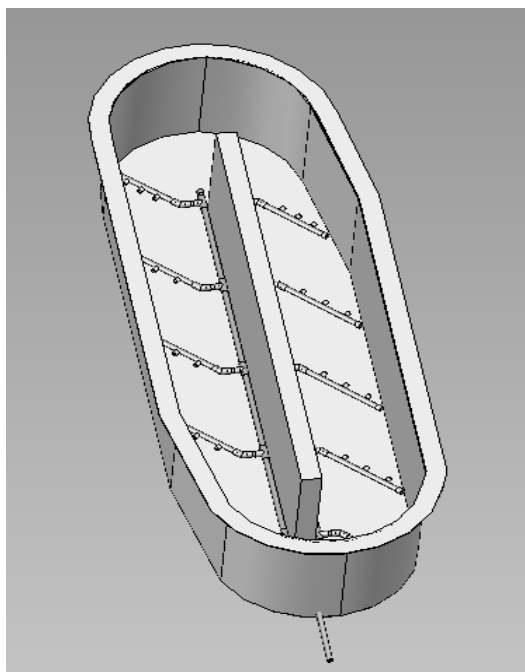


Figure 5.2.1: CO₂ Supply System

The determination of the volumetric coefficient of oxygen transfer ($k_L a_{O_2}$) was performed according to the methodology proposed by Schmidell (2001) [8]. The method is based on the reduction of dissolved oxygen concentration by addition of sodium sulfite (Na_2SO_3). Subsequently, air injection is performed under the conditions to be evaluated and the measure of the dissolved oxygen concentration is monitored.

The determination of the coefficient of volumetric transfer of carbon dioxide ($k_L a_{CO_2}$) was performed according to the methodology proposed by Talbot (1990) [10]. The author determined the relationship between $k_L a_{CO_2}$ and $k_L a_{O_2}$ by Equation 5.2.9.

$$k_L a_{CO_2} = k_L a_{O_2} * \sqrt{\frac{D_{O_2}}{D_{CO_2}}} \quad \text{Equation 5.2.9}$$

Analytical determinations

The pH was determined with a digital pH meter (QUIMIS Q400H, Brazil).

108 Measurements of dissolved oxygen concentration were guided using a
109 dissolved oxygen meter (Orion Model 510A, USA) at 25 °C.

110 RESULTS AND DISCUSSION

111 Isolating H^+ in Equation 5.2.10:

$$112 \quad K_1 = \frac{H^+ \cdot HCO_3^-}{H_2CO_3^*} \quad \text{Equation 5.2.10}$$

113 Where:

$$114 \quad HCO_3^- = \alpha_1 * CT \quad \text{Equation 5.2.11}$$

115 In which:

$$116 \quad \alpha_1 = \frac{1}{\left(1 + \left(\frac{H^+}{K_1}\right) + \frac{K_2}{H^+}\right)} \quad \text{Equation 5.2.12}$$

117 Correlating the pH variation with the variation in CO_2 concentration in
118 the medium (through equations of equilibrium constants), considering that the
119 concentration of HCO_3^- does not vary significantly at each time interval and
120 that $H_2CO_3^*$ represents the sum of the concentration of CO_2 and H_2CO_3 , with
121 the concentration of CO_2 being approximately 250 times greater than H_2CO_3
122 [2], so $H_2CO_3^*$ was regarded as the CO_2 concentration in the liquid medium.
123 Thus replacing the right side of Equations 5.2.11 and 5.2.12 in Equation
124 5.2.10, one arrives at Equation 5.2.13:

$$125 \quad H_t^+ = H_0^+ + \frac{K_1 * (CO_2 - CO_2^0)}{\left(\frac{1}{\left(1 + \frac{H_0^+}{K_1}\right) + \frac{K_2}{H_0^+}}\right) * CT_t} \quad \text{equation 5.2.13}$$

126 Considering that during the injection of CO₂ in the liquid medium, the mass
127 balance for this component may be given by Equation 5.2.14, values of CO₂
128 as a function of time (Figure 5.2.2) were plotted.

$$129 \quad \frac{dCO_2}{dt} = k_L a \cdot (CO_2^{Sat} - CO_2) \quad \text{equation 5.2.14}$$

130 where:

131 $k_L a = 96 \text{ d}^{-1}$ (determined experimentally)

132 CO_2^{Sat} - CO₂ concentration at saturation with the gas phase
133 that represents parts of CO₂ in parts of H₂O [4].

$$134 \quad CO_2^{Sat} = \left(\frac{x_{CO_2}}{1 - x_{CO_2}} \right) * \left(\frac{M_{CO_2}}{M_w} \right) \quad \text{equation 5.2.15}$$

135 where:

136 x_{CO_2} - Molar fraction of CO₂ in the saturated medium

$$137 \quad x_{CO_2} = \frac{p_{CO_2}}{H_{CO_2}} \quad \text{equation 5.2.16}$$

138 p_{CO_2} - Partial pressure of CO₂ in the saturated medium (atm)

139 H_{CO_2} - Henry constant for CO₂ at medium temperature (atm⁻¹)

140 M_{CO_2} - Molar mass of CO₂ (44)

141 M_w - Molar mass of water (18)

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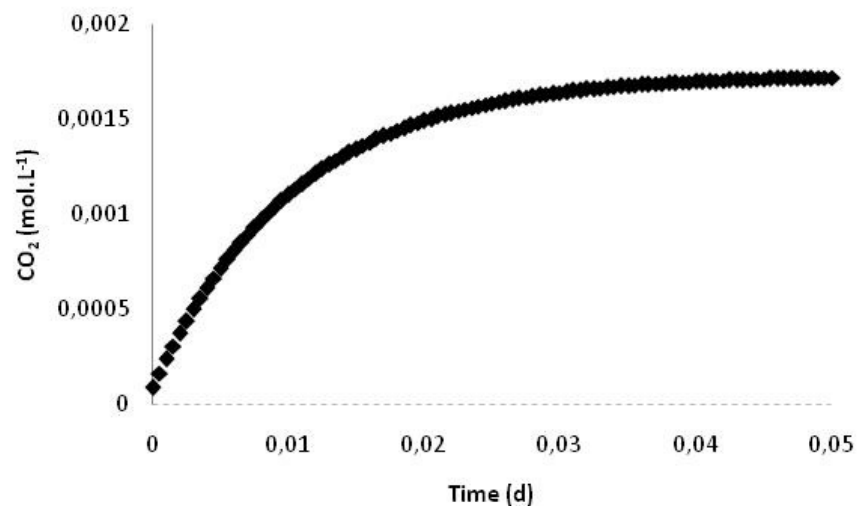


Figure 5.2.2: CO₂ concentration in the medium as a function of time

In order to validate the proposed equation, pH values versus time obtained from Equation 5.2.13 and the values obtained experimentally during the injection of CO₂ into the medium were plotted. Figure 5.2.3 shows the values simulated from Equation 5.2.13 and observed experimentally for pH versus time.

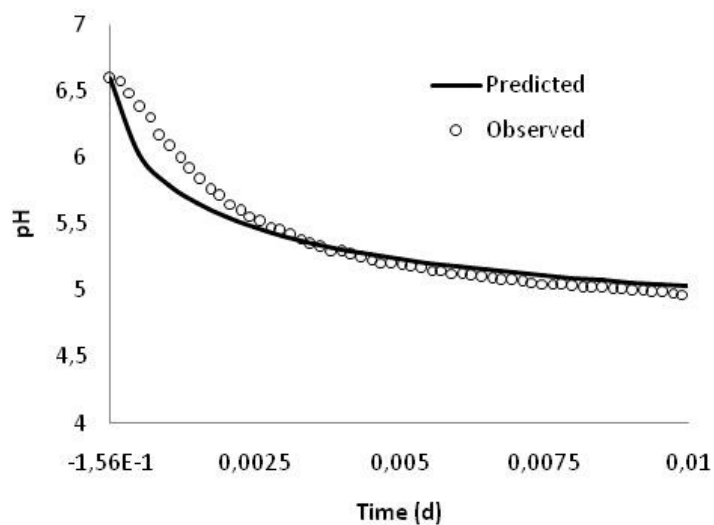


Figure 5.2.3: pH values versus time during the supply of CO₂ in the medium

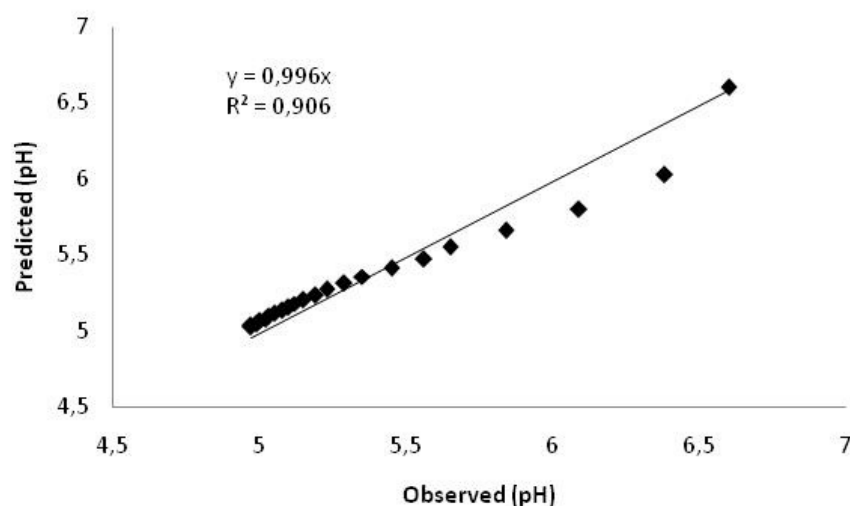
Grima et al. (1999) [3] established an equation for the transfer of CO₂ in tubular photobioreactors. These authors confirmed the application of the

theory of the liquid film when CO₂ is injected into seawater through an air-lift CO₂ supplysystem.

Talbot et al. (1991) [10] concluded that the physico-chemical conditions presented in algal biomass culture medium (presence of OH⁻, H₂O and NH₃) did not significantly affect the coefficient of mass transfer of CO₂, their reactions can be neglected. Thus, they determined that the volumetric coefficient of mass transfer of CO₂ (k_{LaCO_2}) can be calculated from the k_{LaO_2} by a correction factor involving the diffusivity of both gases in water.

Putt et al. (2011) [5] developed an absorption column in order to absorb 90% of supplied CO₂. These authors concluded that the best results obtained (82%) occurred in media containing low alkalinity (pH 8-9).

Figure 5.2.4 shows the values predicted by Equation 13 as a function of the experimentally observed values



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Figure 5.2.4: values predicted by Equation 5.2.13 according to the experimentally observed pH values

Figure 5.2.5 shows simulated values of pH versus time at different initial conditions for the total dissolved inorganic carbon, pH and CO₂.

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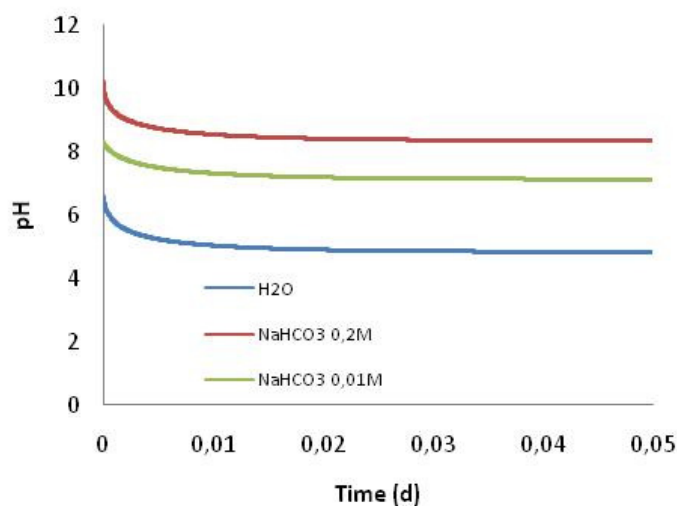


Figure 5.2.5 pH versus time (values simulated from Equation 13)

To make the microalgal growth viable at satisfactory rates it is necessary to maintain the pH within the ideal range, specific for each microorganism. According to Benemann et al. (1978) [1] buffering the system with respect to CO₂ injection system depends on the range of variation of pH. The buffering capacity is at a minimum at about pH 8.3 where the bicarbonate is the dominant species. In both, it increases above and below this region, though at a higher rate in the acidic region. Thus, algae having the ability to grow in media with pH between 6 and 7.5 require less alkalinity for the same carbon storage. Furthermore, the fraction of the total inorganic carbon in the form of carbonate decreases approximately at a factor of 10 for every decrease in one pH unit (between pH 7 to 10). On the other hand, the fraction of CO₂ decreases 10 times with each increase in pH in this range, tending to minimize problems with loss of CO₂ to the atmosphere at high pH.

CONCLUSIONS

The results show that it is possible to determine the behavior of pH from CO₂ values. In processes of CO₂ biofixation, the relation between the variation of CO₂ and variation in the pH of the medium makes it possible to establish control of these factors.

The determination of the volumetric mass transfer coefficient for the gas injection system used in a CO₂ biofixation processes can be performed based on the values obtained for oxygen.

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