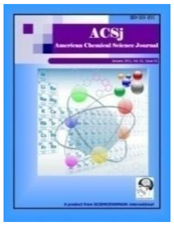

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Relation between Transfer of CO_2 and the pH of the Medium

Jorge Alberto Vieira Costa[1] and Felipe Vieira Camerini[1*]

[1]Federal University of Rio Grande, College of Chemistry and Food Engineering, Laboratory of Biochemical Engineering, Brazil.

Authors' contributions

This work was carried out in collaboration between all authors. Author JAVC designed the study and managed the literature searches. Author FVC managed the analyses, performed the statistical analysis and wrote the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Microalgae are great users of CO_2 and can fix large amounts of this compound. In algal biomass production systems, the requirement of carbon is usually supplied by CO_2, 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 CO_2 concentration and the pH of the medium and validate the equation proposed for the transfer of CO_2 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 performed in a 200 L open raceway type bioreactor, in which a gas injection system was used where air enriched with 12% $CO_{2\ (V/V)}$ at a specific flow rate of 0.05 min^{-1}. An equation was established to determine the pH variation from the variation of the CO_2 concentration in the environment. The data obtained from the proposed equation were satisfactorily explained by experimental data ($r^2 = 0.90$).

Keywords: CO_2; supply; pH; microalgae.

**Corresponding author: E-mail: felipecamerini@gmail.com;*

1. INTRODUCTION

The photoautotrophic growth of microalgae requires the supply of CO_2 as a carbon source. At the same time, the supply of CO_2 helps to control the pH of the culture. Chemical analyses show that microalgal biomass contains 40 to 50% of carbon, which suggests that approximately 1.5 to 2.0 kg of carbon dioxide is needed to produce 1.0 kg of biomass [9].

The transfer of CO_2 into the culture medium is a factor that has been gaining attention in studies in chemical and biochemical engineering. Theoretical and experimental correlations have been well developed. However, they only provide approximate and/or relative estimates of transfer rates. In the final analysis, these rates must be empirically determined from prototypes and pilots. This is especially true for the carbonation of open ponds, where instances of irregular surfaces are frequent due to turbulence, wind and bubbles. These disturbances may cause a significant effect on gas transfer in tanks [1].

The generally used explanation for the mechanism of gas transfer is the dual-film theory. According to this theory, there are two films, a liquid and a gas, the gas-liquid interface promotes most of the resistance against the passage of gas molecules from the gas phase to the liquid phase. For high solubility gases in the liquid phase, for example, absorption of SO_2 in water, the main absorption resistance is offered by the gas film. For low solubility gases in the liquid phase, for example, absorption of oxygen and CO_2 in aqueous solutions, the resistance is limited by the liquid film. For intermediate solubility gases, both films can offer significant resistance [6].

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

$$CO_2 + OH^- \xleftrightarrow{k} HCO_3^-$$
$$CO_2 + H_2O \xleftrightarrow{k} HCO_3^- + H^+$$
$$HCO_3^- + OH^- \xleftrightarrow{k} CO_3^{2-} + H_2O$$
$$HCO_3^- \xleftrightarrow{k} CO_3^{2-} + H^+$$
$$H_2O \xleftrightarrow{k} H^+ + OH^-$$

The relationship between the chemical species of inorganic carbon and pH of the medium may be expressed by the dissociation constants K_1 and K_2, shown in Equations 1 and 2.

$$K_1 = \frac{H^+ \cdot HCO_3^-}{H_2CO_3{}^*} \qquad \text{Equation 1}$$

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

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

$$K_1 = 4{,}4361x10^{-7}$$
$$K_2 = 4{,}6881x10^{-11}$$

$$\alpha_0 = \frac{1}{\left(1 + \left(\frac{K_1}{H^+}\right) + \frac{K_1K_2}{H^{+2}}\right)} \qquad \text{Equation 3}$$

$$\alpha_1 = \frac{1}{\left(1 + \left(\frac{H^+}{K_1}\right) + \frac{K_2}{H^+}\right)} \qquad \text{Equation 4}$$

$$\alpha_2 = \frac{1}{\left(1 + \left(\frac{H^{+2}}{K_1K_2}\right) + \frac{H^+}{K_2}\right)} \qquad \text{Equation 5}$$

$$CO_2 = \alpha_0 * CT \qquad \text{Equation 6}$$

$$HCO_3^- = \alpha_1 * CT \qquad \text{Equation 7}$$

$$CO_3^{-2} = \alpha_2 * CT \qquad \text{Equation 8}$$

Where CT is the total concentration of inorganic carbon in the medium.

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

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

2. MATERIALS AND METHODS

2.1 CO_2 Supply System

The determinations of the CO_2 global transfer coefficient (k_La_{CO2}) were performed in an open raceway bioreactor (2.50 x 0.70 x 0.40 m) with 200 L volume capacity, in which a gas injection system was used (Fig. 1) where enriched air with 12% $CO_{2\ (V/V)}$ was injected into the medium at a specific flow rate 0.05 min^{-1}. This system was used to provide a homogeneous distribution of the mass transferred to the liquid medium (fresh water in this case).

The determination of the volumetric coefficient of oxygen transfer (k_La_{O2}) 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 measure dissolved oxygen concentration.

The determination of the coefficient of volumetric transfer of carbon dioxide (k_La_{CO2}) was performed according to the methodology proposed by Talbot (1990) [10]. The author determined the relationship between k_La_{CO2} and k_La_{O2} by Equation 9 [11].

$$k_L a_{CO_2} = k_L a_{O_2} * \sqrt{\frac{D_{O_2}}{D_{CO_2}}} \qquad \text{Equation 9}$$

2.2 Analytical Determinations

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

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

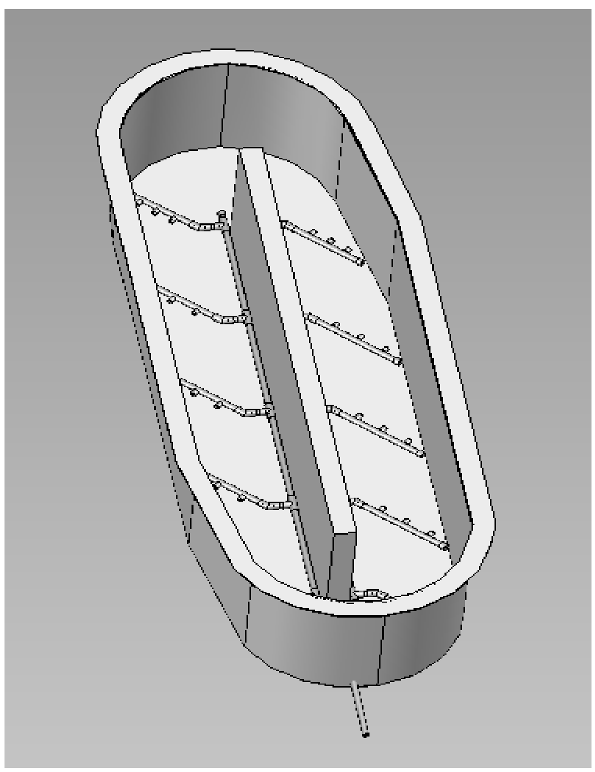

Fig. 1. CO_2 Supply System

3. RESULTS AND DISCUSSION

Isolating H^+ in Equation 10:

$$K_1 = \frac{H^+ \cdot HCO_3^-}{H_2CO_3^*} \quad \text{Equation 10}$$

Where:

$$HCO_3^- = \alpha_1 * CT \quad \text{Equation 11}$$

In which:

$$\alpha_1 = \frac{1}{\left(1 + \left(\frac{H^+}{K_1}\right) + \frac{K_2}{H^+}\right)} \quad \text{Equation 12}$$

Correlating the pH variation with the variation in CO_2 concentration, considering that the concentration of HCO_3^- does not vary significantly at each time interval and that $H_2CO_3^*$ represents the sum of the concentration of CO_2 and H_2CO_3, with the concentration of CO_2 being approximately 250 times greater than H_2CO_3 [2], so $H_2CO_3^*$ was regarded as the CO_2 concentration in the liquid medium. Thus, replacing the right side of Equations 11 and 12 in Equation 10:

$$H_t^+ = H_0^+ + \frac{K_1 * (CO_2 - CO_2^0)}{\left(\frac{1}{\left(1 + \frac{H_0^+}{K_1}\right) + \frac{K_2}{H_0^+}}\right) * CT_t} \quad \text{Equation 13}$$

Considering that during the injection of CO_2 in the liquid medium, the mass balance for this component may be given by Equation 14, values of CO_2 as a function of time (Fig. 2) were plotted.

$$\frac{dCO_2}{dt} = kla \cdot (CO_2^{Sat} - CO_2) \quad \text{Equation 14}$$

Where:

k_La= 96 d^{-1} (determined experimentally)

CO_2^{Sat} - CO_2 concentration at saturation with the gas phase that represents parts of CO_2 in parts of H_2O [4].

$$CO_2^{Sat} = \left(\frac{x_{CO_2}}{1 - x_{CO_2}}\right) * \left(\frac{M_{CO_2}}{M_W}\right) \quad \text{Equation 15}$$

Where:

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

$$x_{CO2} = \frac{p_{CO_2}}{H_{CO_2}} \quad \text{Equation 16}$$

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

H_{CO_2} - Henry constant for CO_2at medium temperature (atm^{-1})

M_{CO_2} - Molar mass of CO_2 (44)

M_W - Molar mass of water (18)

In order to validate the proposed equation, pH values versus time obtained from Equation 13 and the values obtained experimentally during the injection of CO_2 into the medium were plotted. Fig. 3 shows the values simulated from Equation 13 and observed experimentally for pH versus time.

Grima et al. [3] established an equation for the transfer of CO_2 in tubular photobioreactors. These authors confirmed the application of the theory of the liquid film when CO_2 is injected into seawater through an air-lift CO_2 supply system.

Talbot et al. [10] concluded that the physico-chemical conditions presented in algal biomass culture medium (presence of OH^-, H_2O and NH_3) did not significantly affect the coefficient of mass transfer of CO_2, their reactions can be neglected. Thus, they determined that the volumetric coefficient of mass transfer of CO_2 (k_La_{CO2}) can be calculated from the k_La_{O2} by a correction factor involving the diffusivity of both gases in water.

Putt et al. [5] developed an absorption column in order to absorb 90% of supplied CO_2. These authors concluded that the best results obtained (82%) occurred in media containing low alkalinity (pH 8-9).

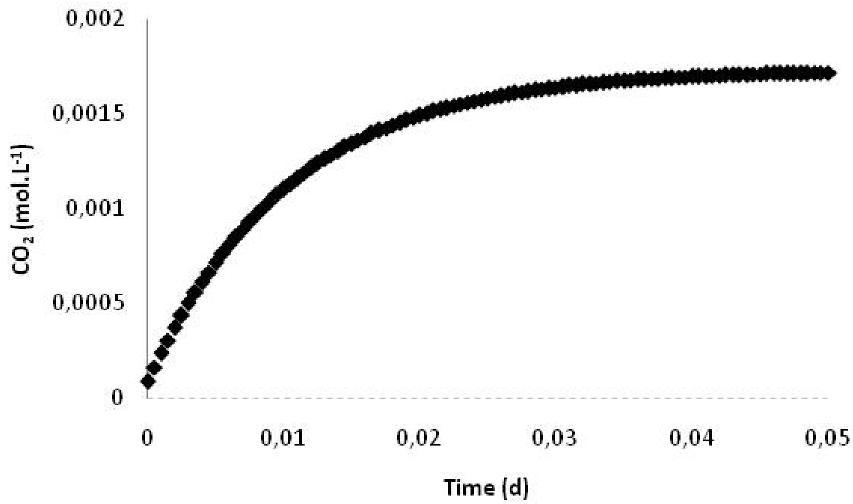

Fig. 2. CO_2 concentration in the medium as a function of time

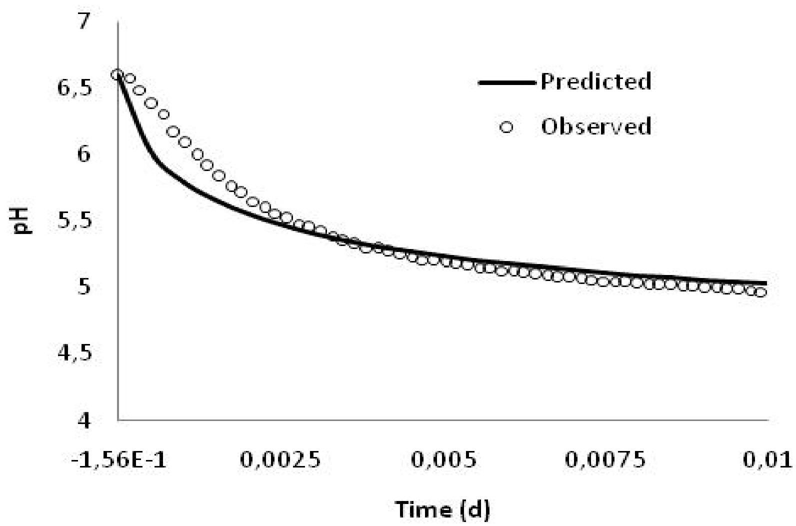

Fig. 3. pH values versus time during the supply of CO_2 in the medium

Fig. 4 shows the values predicted by Equation 13 as a function of the experimentally observed values.

Fig. 5 shows simulated values of pH versus time at different initial conditions for the total dissolved inorganic carbon, pH and CO_2.

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. [1], buffering the system with respect to CO_2 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 CO_2 decreases 10 times with each increase in pH in this range, tending to minimize problems with loss of CO_2 to the atmosphere at high pH.

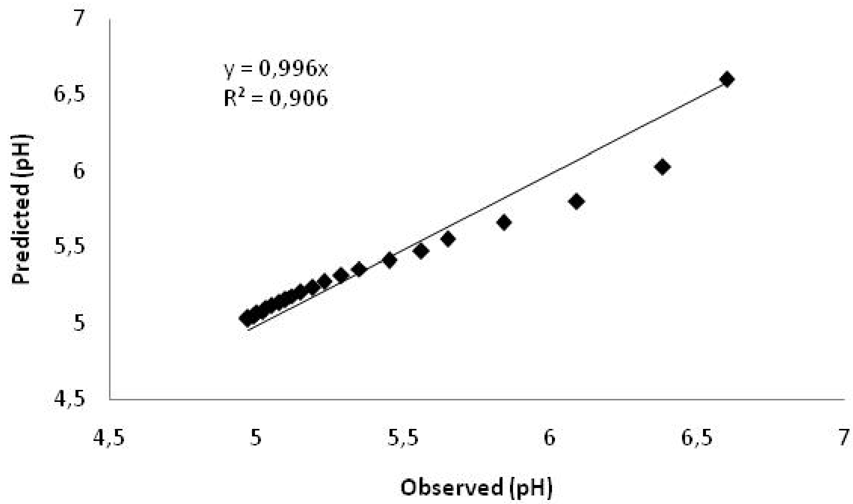

Fig. 4. Values predicted by equation 13 according to the experimentally observed pH values

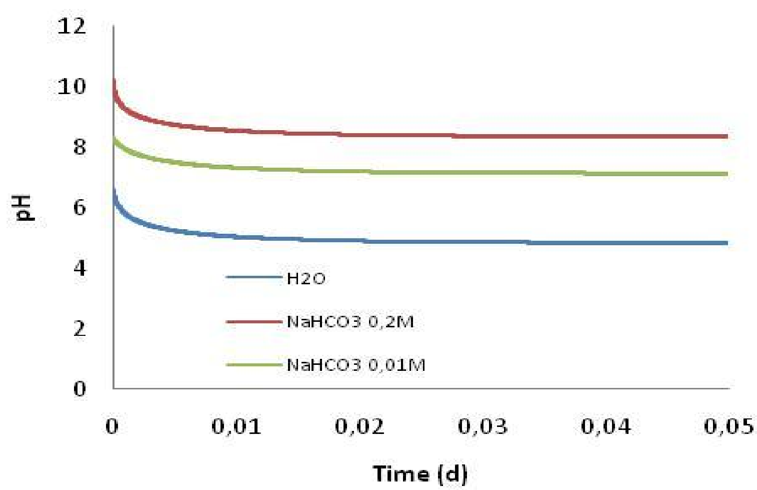

Fig. 5. pH versus time (values simulated from equation 13)

4. CONCLUSIONS

The results show that it is possible to determine the behavior of pH from CO_2 values. In processes of CO_2 biofixation, the relation between the variation of CO_2 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 CO_2 biofixation processes can be performed based on the values obtained for oxygen.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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