

## GENERAL RESEARCH

## Carbon Dioxide Stripping In Bubbled Columns

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The carbonate buffer system plays a fundamental role in the biological treatments of wastewaters. In this work, the CO<sub>2</sub> volumetric mass transfer coefficient ( $k_{L}a_c$ ) in a bubbled column was determined using the conventional titration method for different column volumes and air flow rates. In addition, a simple method to determine  $k_{L}a_c$  based on the interpretation of the changes in the pH level due to the CO<sub>2</sub> stripping was developed. Results show that the apparent CO<sub>2</sub> volumetric mass transfer coefficient ( $k_{L}a_{c-app}$ ) was strongly affected by the pH level; however, the actual CO<sub>2</sub> volumetric mass transfer coefficient,  $k_{L}a_c = k_{L}a_{c-app}/\alpha_0$ , was constant within the tested pH conditions. In addition,  $k_{L}a_c$  increased with higher air flow rates and lower column volumes; the obtained  $k_{L}a_c$  values ranged between 20.0 and 71.9 h<sup>-1</sup>. For all the tested conditions,  $k_{L}a_c$  values obtained using the noncontrolled pH method were similar to the values measured using the titrimetric method. The proposed mathematical model represented adequately the changes on the pH level and total inorganic carbon species concentration as a function of time. The model was extended to take into account the effect of phosphates. Simulation results showed that, although phosphates buffered the changes of pH, the losses of total inorganic carbon were faster than in the case of a nonbuffered solution; thus, the rise in the pH level prevented the stripping of CO<sub>2</sub>.

## Introduction

The carbonate buffer system plays a fundamental role in the biological treatments of wastewaters. This system is present in all the cases, and its buffer capacity depends on the balance between the processes of generation and consumption of inorganic carbon. Among the first ones, microbial (aerobic or anoxic) respiration and transport from the gaseous phase can be mentioned. On the other hand, the main processes that determine the decrease of CO<sub>2</sub> concentration are the nitrification process (due to assimilation of the CO<sub>2</sub>) and losses due to the transport toward the gaseous phase, a process known as stripping.<sup>1–3</sup>

The determination of the carbon dioxide transfer rate is crucial given the close relationship between biological and physico-chemical processes and the concentration of CO<sub>2</sub> in solution. For example, it is clear that the nitrification of extremely concentrated ammonia wastewaters requires sufficient alkalinity to buffer the protons generated during the process and bicarbonate as the carbon source for the autotrophic biomass. However, low pH values and high aeration conditions cause a decrease of the available inorganic carbon due to the stripping of CO<sub>2</sub>.<sup>4,5</sup> In addition, model studies have pointed out the importance of pH on the inorganic carbon limitation of algal biofilm growth.<sup>6</sup> On the contrary, when the CO<sub>2</sub> stripping rate is lower than its production rate (e.g., using low agitation and/or aeration conditions), the dissolved CO<sub>2</sub> concentration rises above the saturation value (CO<sub>2,sat</sub>).<sup>7</sup> In this case, wastewaters with high concentrations of Ca<sup>2+</sup> and/or Mg<sup>+</sup> lead to the formation of highly insoluble carbonates.<sup>8</sup> Although the carbon dioxide mass transfer coefficient is an important feature of reactor design, few direct measurements were reported.<sup>9,10</sup> Instead,

researchers commonly assume that the carbon dioxide mass transfer coefficient can be estimated using values for oxygen mass transfer coefficients that have been extensively measured.<sup>11</sup>

Titrimetry is a well-established technique to monitor (bio)chemical reactions that affects the pH of the medium. This technique was successfully applied to evaluate different pHs affecting processes such as nitrification, denitrification, and aerobic carbon oxidation.<sup>1,2,12</sup> Titrimetric sensors require a pH controller to maintain the pH value at a constant set point through the addition of a strong acid or base concentrated solution using a peristaltic pump. In this work, the CO<sub>2</sub> volumetric mass transfer coefficient ( $k_{L}a_c$ ) in a bubbled column was determined using the conventional titration method for different column volumes and air flow rates. In addition, a simple method to determine  $k_{L}a_c$  based on the interpretation of the changes in the pH level due to the CO<sub>2</sub> stripping was developed, and the results were compared with the titration method.

## Theory

The carbonate buffer system consists of four species: dissolved CO<sub>2</sub> (CO<sub>2d</sub>), carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), and carbonate (CO<sub>3</sub><sup>2-</sup>). At room temperature (25 °C), the ratio (CO<sub>2</sub> dissolved)/H<sub>2</sub>CO<sub>3</sub> is 99.76:0.24, and it is independent of pH and ionic strength.<sup>8</sup> These two species can be dealt with as a single combined one, CO<sub>2</sub><sup>\*</sup>, with little error:<sup>13</sup>

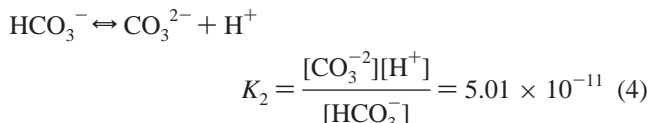
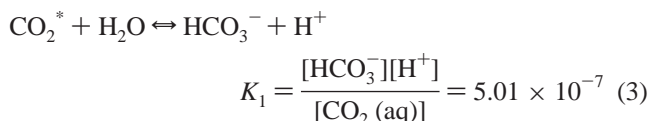


The CO<sub>2</sub><sup>\*</sup> tends to equilibrium with the partial pressure of CO<sub>2</sub> (gas) outside the liquid:

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The low partial pressure of atmospheric  $\text{CO}_2$  limits the  $\text{CO}_2$  concentration of the solution according to Henry's law. Thus, air bubbles strip more inorganic carbon than they can transfer into the water, shifting the following equilibria,



where  $K_1$  and  $K_2$  values correspond to an operation temperature of 25 °C.<sup>14</sup> As the  $\text{CO}_2$  is stripped from the solution, these equilibria are shifting to the left, increasing the pH level. In comparison to gas-liquid transport phenomena (eq 2), acid/base reactions involving  $\text{CO}_2^*$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  are extremely rapid. Even the hydration of  $\text{CO}_2$ , which is considerably slower than the acid/base reactions, is significantly faster than the physical transfer process.<sup>3,9</sup> Thus, gas-liquid mass transfer can be considered as the rate-limiting reaction step, and acid/base reactions can be assumed as near the equilibrium conditions.

In order to describe the  $\text{CO}_2$  stripping process due to the aeration, a semiempirical approach with a lumped stripping parameter is inevitable. The liquid-mass balance for the total soluble inorganic carbon ( $C_T = \text{CO}_2^* + \text{CO}_3\text{H}^- + \text{CO}_3^{2-}$ ) at a constant temperature, pressure, and volume under constant partial pressure of  $\text{CO}_2$  in the gas phase is<sup>5,7</sup>

$$\frac{dC_T}{dt} = k_L a_c (\text{CO}_{2\text{sat}} - \text{CO}_2^*) \quad (5)$$

where  $k_L a_c$  ( $\text{h}^{-1}$ ) is the volumetric mass transfer coefficient for  $\text{CO}_2$ , and  $\text{CO}_{2\text{sat}}$  is the equilibrium value that depends on the partial pressure of carbon dioxide. If 1 atm of pressure of air (with 0.037% of  $\text{CO}_2$ ) is assumed, then the value of  $\text{CO}_{2\text{sat}}$  is  $\sim 0.01$  mM.<sup>14</sup>

The concentration of each inorganic carbon species ( $\text{CO}_2^*$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) can be calculated as a function of pH considering the acid/base equations and the total inorganic carbon species concentration ( $C_T$ ):

$$\text{CO}_2^* = \alpha_0 C_T = \frac{H^2}{H^2 + K_1 H + K_1 K_2} C_T \quad (6)$$

$$\text{HCO}_3^- = \alpha_1 C_T = \frac{K_1 H}{H^2 + K_1 H + K_1 K_2} C_T \quad (7)$$

$$\text{CO}_3^{2-} = \alpha_2 C_T = \frac{K_1 K_2}{H^2 + K_1 H + K_1 K_2} C_T \quad (8)$$

Considering only the buffer systems of inorganic carbon compounds ( $\text{CO}_2^*$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) and water, the charge balance equation of ionic species in the liquid phase is

$$\text{H}^+ + Z = \text{OH}^- + \text{HCO}_3^- + 2\text{CO}_3^{2-} \quad (9)$$

where  $Z$  (=cations - anions) is the total concentration of inert

species (e.g., strong acids/bases).<sup>15,16</sup> By combination of eqs 7-9, the following is obtained,

$$\text{H}^+ + Z = \frac{K_w}{\text{H}^+} + (\alpha_1 + 2\alpha_2) C_T \quad (10)$$

where  $K_w$  ( $=1 \times 10^{-14}$ ) is the dissociation constant of water. The solution of eq 10 provides the pH value as a function of  $C_T$  or the  $C_T$  value for a given pH, depending on the available data. Thus, two operating modes can be employed to determine the value of  $k_L a_c$ : (i) controlled pH (titrimetry) or (ii) noncontrolled pH methods.

**(i) Controlled pH method—Titrimetry.** In this method, a pH control device is used to maintain the pH value at a constant set point through the addition of a strong acid (AH) concentrated solution using a peristaltic pump.<sup>12</sup> Because the pH value is constant,  $\alpha_0$  is constant; thus, eq 5 can be integrated to obtain the following expression,

$$C_T = C_{T0} - (C_{T0} - C_{T\text{sat}}) e^{-k_L a_c \text{app} t} \quad (11)$$

where  $C_{T0} = \text{CO}_{2\text{sat}} / \alpha_0$  is the total inorganic carbon species at saturation conditions and  $k_L a_c \text{app} = \alpha_0 k_L a_c$ , is the apparent  $\text{CO}_2$  volumetric mass transfer coefficient at the experimental pH level. If  $A^-$  is the anion concentration corresponding to the added acid, then the charge balance equation results:

$$A^- = \text{H}^+ + Z - \frac{K_w}{\text{H}^+} - (\alpha_1 + 2\alpha_2) C_T \quad (12)$$

By combination of expressions 11 and 12 and taking into account that  $A^- = 0$  when  $t = 0$ , the following is obtained:

$$A^- = (\alpha_1 + 2\alpha_2)(C_{T0} - C_T)(1 - e^{-k_L a_c \text{app} t}) \quad (13)$$

The added anion concentration ( $A^-$ ) can be estimated knowing the concentration of the stock solution of acid ( $A_{ST}$ ), the reactor volume ( $V_R$ ), the flow rate of the peristaltic pump ( $Q_P$ ), and the cumulative pumping time ( $t_p$ ),

$$A^- = \frac{t_p Q_P A_{ST}}{V_R} \quad (14)$$

and the combination of expressions 13 and 14 leads to the following:

$$t_p = \left[ \frac{V_R (\alpha_1 + 2\alpha_2) (C_{T0} - C_T)}{Q_P A_{ST}} \right] (1 - e^{-k_L a_c \text{app} t}) \quad (15)$$

Therefore, by monitoring the cumulative pumping time ( $t_p$ ) to keep the pH constant as a function of the process time ( $t$ ), the value of  $k_L a_c \text{app}$  can be calculated using eq 15. The applicability of this method depends upon the first term in brackets on the right-hand side; if this term is constant, then eq 15 can be used to estimate the value of  $k_L a_c \text{app}$ .

**(ii) Noncontrolled pH Method.** If the pH is not controlled, the pH increases as a function of time ( $t$ ) due to the  $\text{CO}_2$  stripping process. For a solution with known values of  $C_{T0}$  and  $\text{pH}_0$  (e.g., a freshly prepared pH-adjusted bicarbonate solution), the total concentration of inert species ( $Z$ ) can be calculated by reordering eq 10,

$$Z = \frac{K_w}{\text{H}_0^+} + (\alpha_{10} + 2\alpha_{20}) C_{T0} - \text{H}_0^+ \quad (16)$$

where the subscripts "o" indicate the values at pH<sub>o</sub>. Because Z represents nonvolatile acids or bases, this term is constant; thus, C<sub>T</sub> values can be calculated as a function of pH, reordering the charge balance equation:

$$C_T = \frac{H^+ + Z - \frac{K_w}{H^+}}{\alpha_1 + 2\alpha_2} \quad (17)$$

If the variations of pH and C<sub>T</sub> as a function of time are known, CO<sub>2</sub>\* can be calculated using eq 6. In addition, the stripping rate ( $-dC_T/dt$ ) can be estimated from the plot of C<sub>T</sub> as a function of time using a moving regression window, for example. Finally, by plotting  $dC_T/dt$  versus the CO<sub>2</sub>\* concentration, the value of  $k_{La_c}$  can be estimated from the slope of the obtained line (eq 5).

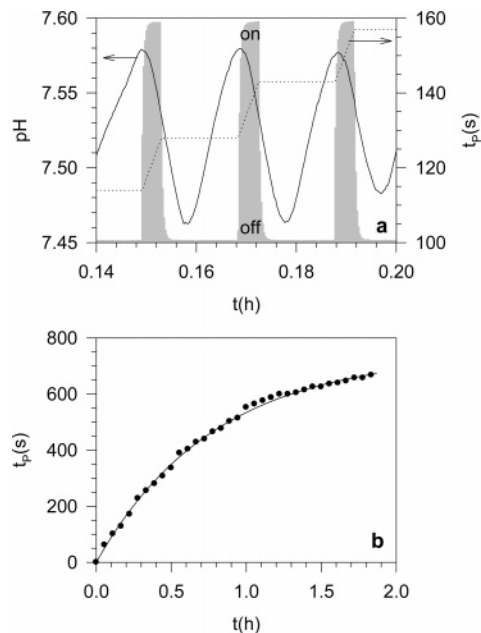
### Experimental Section

Carbon dioxide stripping experiments were conducted in a bubbled column (33 mm internal diameter × 700 mm height) with a maximum working volume of 500 mL. Air was introduced by passing through a glass fritter (40–60 μm pores) installed at the bottom of the column. Air was set to stable flow rates (0.5–1.0 L/min) using a high-precision rotameter (Bruno Schilling model MB 60V, Argentina). External recirculated flow by a peristaltic pump (Apema model AP20, Argentina) from the bottom to the top of the column was used to achieve homogeneous mixing of the solution; in all cases, the flow rate was 230 mL/min. The pH of the recirculation line was measured continuously using a polymer body pH probe (Broadley-James Corp.) connected to an on/off pH controller (Masstek, Argentina). The pH of the column was corrected using sulfuric acid (1 N). An 8-bit analogic/digital (A/D) converter (Biloba Ingenieria model BLB 2.0, Argentina) was used to obtain the output signal (4–20 mA) from the pH controller. The on/off control signal actuating the acid pump (Apema model AP25 0.3-M-S, Argentina) was converted to 500 mV or null signal and connected to a digital input/output (I/O) module (Biloba Ingenieria, Argentina). Both the A/D converter and the digital I/O module were connected to a personal computer via an RS232 protocol.

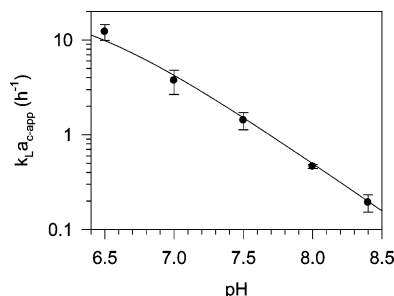
Sodium bicarbonate (with purity > 99.7%) purchased from a local supplier (Anedra, Argentina) was used to prepare solutions of known total inorganic carbon concentration (C<sub>T</sub>); the different initial pH values were obtained by adding sulfuric acid (2 N). In all cases, deionized water was used. All the stripping assays were conducted at room temperature (23 ± 2 °C).

### Results and Discussion

**(i) Controlled pH method—Titrimetry.** A typical example of the results obtained during a carbon dioxide stripping experiment using the pH control device is shown in Figure 1. The obtained pH pattern was due to the on/off control-type feeding of the concentrated acid solution to avoid dilution problems. Accordingly, the pH of the medium was not exactly constant, but it fluctuated around the set point (Figure 1a). Figure 1b shows that the cumulative pumping time ( $t_p$ ) increased as a function of the process time ( $t$ ), reaching a maximum value at ~2 h of operation. The observed staircase pattern of the cumulative pumping time was the result of the on/off control-type of the acid pump. From this plot,  $k_{La_{c-app}}$  was calculated by nonlinear regression (Sigma Plot 2.0) using eq 15 (Figure 1b).



**Figure 1.** Typical results obtained during a CO<sub>2</sub> stripping experiment: (a) detail of pH (solid line), cumulative pumping time (dotted line), and the acid pump on/off operation (gray bars) profiles during three pH control cycles; and (b) cumulative pumping time ( $t_p$ ) (circles) as a function of the process time. The line indicates the result obtained by fitting eq 15 to the experimental data.

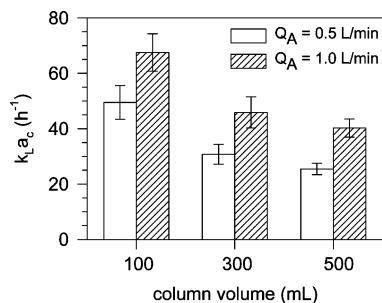


**Figure 2.** Effect of pH on the apparent CO<sub>2</sub> volumetric mass transfer coefficient ( $k_{La_{c-app}}$ ). Error bars indicate the 95% confidence interval. The solid line indicates the calculated value of  $k_{La_{c-app}} = \alpha_0 k_{La_c}$  using  $k_{La_c} = 25.5 \text{ h}^{-1}$  (Table 1). In this case, the column volume was 500 mL and the air flow rate was 0.5 L/min.

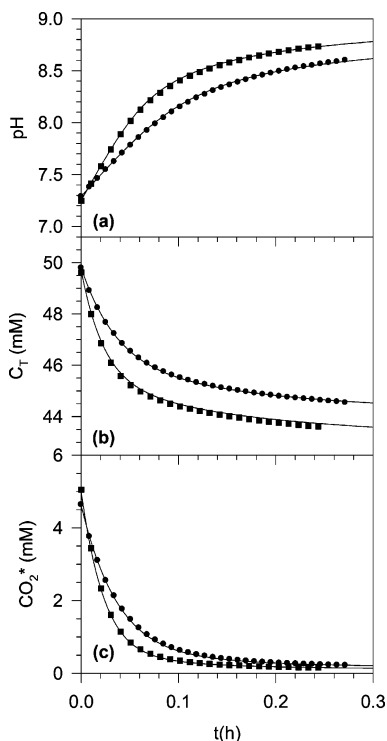
**Table 1. Fraction of the Total Inorganic Carbon Species That is Present as CO<sub>2</sub>\* ( $\alpha_0$ ), Apparent ( $k_{La_{c-app}}$ ) and Actual ( $k_{La_c}$ ) CO<sub>2</sub> Volumetric Mass Transfer Coefficients as a Function of pH (Conditions: Air Flow Rate = 0.5 L/min, Column Volume = 500 mL)**

pH	$\alpha_0$	$k_{La_{c-app}} \text{ (h}^{-1}\text{)}$	$k_{La_c} \text{ (h}^{-1}\text{)}$
6.5	0.3868	12.20 ± 2.32	31.5 ± 6.0
7.0	0.1663	3.73 ± 1.07	22.4 ± 6.4
7.5	0.0593	1.42 ± 0.29	23.9 ± 4.9
8.0	0.0195	0.46 ± 0.02	23.7 ± 1.1
8.4	0.0078	0.19 ± 0.05	24.7 ± 5.1
		mean	25.5 ± 2.1

The obtained results show that the apparent CO<sub>2</sub> volumetric mass transfer coefficient ( $k_{La_{c-app}}$ ) was strongly affected by the pH level (Figure 2);  $k_{La_{c-app}}$  increased from  $0.20 \pm 0.05$  to  $12.20 \pm 2.32 \text{ h}^{-1}$  when the pH decreased from 8.4 to 6.5. For each pH level, the actual CO<sub>2</sub> volumetric mass transfer coefficient was calculated as  $k_{La_c} = k_{La_{c-app}}/\alpha_0$ ; Table 1 shows that  $k_{La_c}$  was constant within the tested pH conditions. Using the average value for  $k_{La_c} = 25.5 \text{ h}^{-1}$ , the apparent  $k_{La_{c-app}}$  value was plotted against the pH level. Figure 2 shows that the calculated  $k_{La_{c-app}}$  values were in accordance with the experimental ones. Thus, the stripping of CO<sub>2</sub> can be adequately



**Figure 3.** Effect of the column volume on the actual  $CO_2$  mass transfer coefficient ( $k_{La_c}$ ) for different air flow rates. Error bars indicate the 95% confidence interval.

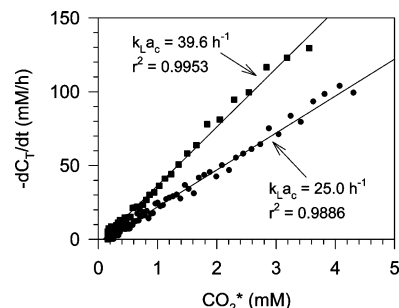


**Figure 4.** Changes in pH (a),  $C_T$  (b), and  $CO_2^*$  (c) as a function of time due to the carbon dioxide stripping under different air flow rates: (circles) 0.5 L/min and (squares) 1.0 L/min. In both cases, the column volume was 500 mL. Lines indicate the calculated values using the proposed model.

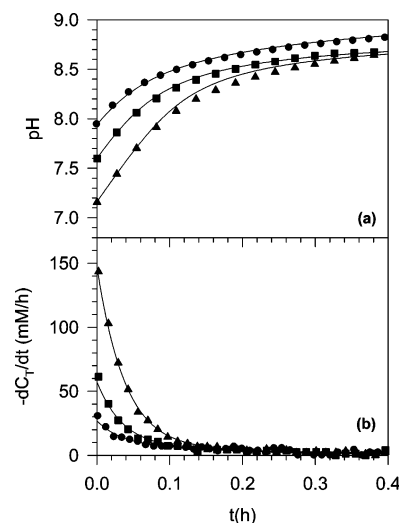
modeled as a function of pH using a single experimental coefficient ( $k_{La_c}$ ), taking into account the effect of the nondissociated acid fraction ( $\alpha_0$ ) on the apparent  $k_{La_c-app}$  value.

Figure 3 shows that  $k_{La_c}$  increased with higher air flow rates ( $Q_A$ ) and lower column volumes ( $V_C$ ); the obtained  $k_{La_c}$  values ranged between 20.0 and 71.9  $h^{-1}$ . The high  $k_{La_c}$  values obtained in the present paper were due to the use of a glass fritter that generated small bubbles at high aeration rates (1–10 vvm). These results were in accordance with those of other authors. For example, Arrua et al.<sup>9</sup> studied the  $CO_2$  stripping of  $Na_2CO_3$  solutions at pH = 9 in stirred tanks; these authors reported that  $k_{La_c}$  values ranged from 18 to 108  $h^{-1}$ . Hill<sup>10</sup> studied the carbon dioxide mass transfer from bubbles to the liquid phase using a gas with 10%  $CO_2$  by volume sparged into a well-mixed baffled reactor; this author found that  $k_{La_c}$  values ranged between 20 and 120  $h^{-1}$ . Sperandio and Paul<sup>11</sup> studied the  $CO_2$  mass transfer from the liquid to the gas phase using an infrared carbon dioxide analyzer; these authors found that  $k_{La_c}$  values ranged between 18.3 and 37.1  $h^{-1}$ .

**(ii) Noncontrolled pH Method.** Typical pH profiles obtained during carbon dioxide stripping experiments without using the



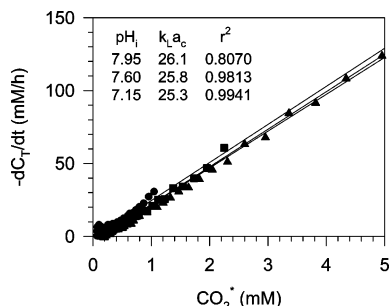
**Figure 5.** Carbon dioxide stripping rate ( $-dC_T/dt$ ) as a function of  $CO_2^*$  under different air flow rates: (circles) 0.5 L/min and (squares) 1.0 L/min. In both cases, the column volume was 500 mL.  $k_{La_c}$  values were estimated from the slopes of the straight lines (eq 5).



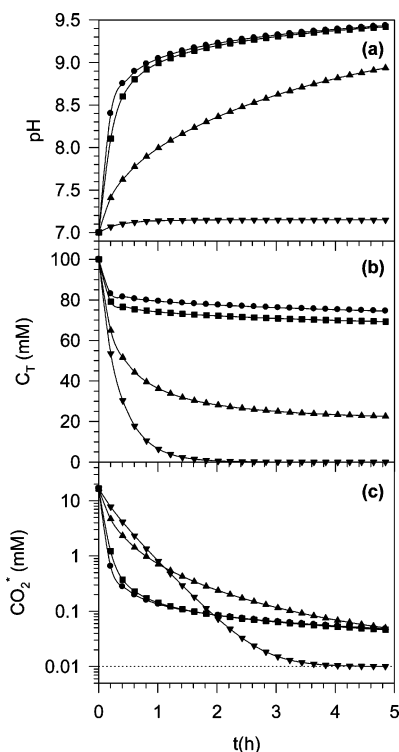
**Figure 6.** Changes in pH (a) and in the  $CO_2$  stripping rate ( $-dC_T/dt$ ) (b) as a function of time for different initial pH values: (circles) pH = 7.95, (squares) pH = 7.60, and (triangles) pH = 7.15. Experimental conditions are as follows: air flow rate = 0.5 L/min and column volume = 500 mL. Lines indicate the calculated values using the proposed model.

pH control device are shown in Figure 4a; in this example, the initial pH was adjusted to 7.25 using sulfuric acid. Within the first 10 min, a fast increase in the pH values was observed (Figure 4a) due to the stripping of  $CO_2$  (Figure 4b). Although  $C_T$  values decrease only 12% (50–44 mM),  $CO_2^*$  decreases ~95% (5–0.2 mM) (Figure 4c), mainly because of the increase of pH. Because  $CO_2^*$  was the actual species that was stripped from the solution, the  $CO_2$  stripping rate decreased as a function of time due to the increase of the pH level. Figure 5 shows that the  $CO_2$  stripping rate increased as a function of the  $CO_2^*$  concentration in accordance with eq 5; thus, from the slope of the obtained straight line, the value of  $k_{La_c}$  was calculated.

For all the tested air flow rates and column volumes,  $k_{La_c}$  values obtained using the noncontrolled pH method were similar to the values measured using the titrimetric method. For example,  $k_{La_c}$  increased from 25.0 to 39.6  $h^{-1}$  with air flow rates of 0.5 and 1.0 L/min, respectively, and a column volume of 500 mL (Figure 5); these values were in accordance with those presented in Figure 3 (titrimetric method) for the same experimental conditions. The results obtained using the titrimetric method showed that  $k_{La_c-app}$  depended on the pH of the solution (Figure 2); this effect is also observed in the noncontrolled pH experiments. As the initial pH decreased, a faster increase of the pH level was observed (Figure 6a) because of a



**Figure 7.** Carbon dioxide stripping rate ( $-dC_T/dt$ ) as a function of  $CO_2^*$  for different initial pH values: (circles) pH = 7.95, (squares) pH = 7.60, and (triangles) pH = 7.15. Experimental conditions are as follows: air flow rate = 0.5 L/min and column volume = 500 mL.



**Figure 8.** Simulation results corresponding to the changes in (a) pH, (b)  $C_T$ , and (c)  $CO_2^*$  as a function of time due to the  $CO_2$  stripping with different total phosphate concentrations: (circles)  $P_T = 0$  M, (squares)  $P_T = 0.01$  M, (triangles facing up)  $P_T = 0.1$  M, and (triangles facing down)  $P_T = 1$  M. In all cases,  $C_{T0} = 100$  mM,  $CO_{2sat} = 0.01$  mM (dotted line), and  $k_{La_c} = 20$  h<sup>-1</sup>.

higher  $CO_2$  stripping rate (Figure 6b); however, the calculated values corresponding to the actual  $k_{La_c}$  were constant (Figure 7). In addition, these values were in accordance with those measured using the controlled pH method for the same experimental conditions (Table 1).

The obtained results demonstrated that the  $CO_2$  stripping process and its effect on the pH can be modeled by solving eqs 5–8, 10, and 16 simultaneously. Therefore, the equation systems were solved using a similar procedure to that developed by Wett and Rauch.<sup>5</sup> Figures 4–7 show that the proposed mathematical model represented adequately the changes on the pH level and the total inorganic carbon concentration ( $C_T$ ) as a function of time due to the stripping of  $CO_2$  from the solution to the gaseous phase for all the tested conditions.

The model can be extended to take into account the effect of other buffer systems (such as phosphate) by means of the incorporation of the corresponding equilibria. For example, if

$P_T$  is the total phosphates concentration in the liquid phase, the charge balance at  $t = 0$  results,

$$Z = \frac{K_w}{H_o^+} + (\alpha_{1o} + 2\alpha_{2o})C_{T0} + (\alpha_{P1o} + 2\alpha_{P2o} + 3\alpha_{P3o})P_T - H_o^+ \quad (18)$$

where  $\alpha_{P1}$ ,  $\alpha_{P2}$ ,  $\alpha_{P3}$  are the fractions of the total phosphates species that are present as  $H_2PO_4^-$ ,  $HPO_4^{2-}$ , and  $PO_4^{3-}$ , respectively. Because these species are nonvolatiles,  $P_T$  is constant; thus, the total inorganic carbon concentration ( $C_T$ ) can be calculated as a function of pH as follows:

$$C_T = \frac{H^+ + Z - \frac{K_w}{H^+} - (\alpha_{P1} + 2\alpha_{P2} + 3\alpha_{P3})P_T}{\alpha_1 + 2\alpha_2} \quad (19)$$

Figure 8 shows the simulation results of the  $CO_2$  stripping in the presence of different phosphate concentrations; in all cases,  $C_{T0} = 100$  mM,  $CO_{2sat} = 0.01$  mM,  $pH_o = 7$ , and  $k_{La_c} = 20$  h<sup>-1</sup>. The pH changes due to the  $CO_2$  stripping process decreased with higher total phosphates concentration (Figure 8a). For example, when  $P_T = 0$ , the pH increased from 7 to 9.44 at  $t = 5$  h; however, for  $P_T = 1$  M, the pH value at this time was 7.15. Although the phosphates buffered the changes of pH, the total inorganic carbon decreased from 74 mM ( $P_T = 0$ ) to 0.08 mM ( $P_T = 1$  M) at  $t = 5$  h (Figure 8b). The raise in the pH level shifted the carbonate equilibria to the dissociated species  $HCO_3^-$  and  $CO_3^{2-}$  and diminished the volatile species concentration  $CO_2^*$  (Figure 8c); thus, this mechanism prevented the stripping of  $CO_2$  from the solution. Simulation results showed that the model can be used to estimate the concentrations of the different inorganic carbon species as a function of time and pH to check the availability of inorganic carbon for nitrification, for example. In addition, the noncontrolled pH method might be easily extended to measure the volumetric mass transfer coefficient of other volatile species such as acetic acid or ammonia.

## Conclusions

The pH strongly affects the apparent  $CO_2$  volumetric mass transfer coefficient ( $k_{La_c-app}$ ); however, the actual  $CO_2$  volumetric mass transfer coefficient  $k_{La_c} = k_{La_c-app}/\alpha_0$  was constant within the tested pH. In addition,  $k_{La_c}$  increased with higher air flow rates ( $Q_A$ ) and lower column volumes ( $V_C$ ). Thus, the stripping of  $CO_2$  can be adequately modeled as a function of pH using a single experimental coefficient ( $k_{La_c}$ ), taking into account the effect of the nondissociated acid fraction ( $\alpha_0$ ).

For all the tested air flow rates and column volumes,  $k_{La_c}$  values obtained using the noncontrolled pH method were similar to the values measured using the titrimetric method. The proposed mathematical model represented adequately the changes on the pH level and total inorganic carbon concentration ( $C_T$ ) as a function of time due to the stripping of  $CO_2$  from the solution to the gaseous phase.

The model was extended to take into account the effect of phosphates by means of the incorporation of the corresponding equilibria. Simulation results showed that, although phosphates buffered the changes of the pH, the losses of total inorganic carbon were faster than in the case of a nonbuffered solution; thus, the raise in the pH level prevented the stripping of  $CO_2$ .

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## Nomenclature

$C_T$  = total inorganic carbon species concentration (M)

$K$  = equilibrium constants of reactions 3 and 4

$K_{La_c}$  = actual  $\text{CO}_2$  volumetric mass transfer coefficient ( $\text{h}^{-1}$ )

$K_{La_c\text{-app}}$  = apparent  $\text{CO}_2$  volumetric mass transfer coefficient ( $\text{h}^{-1}$ )

$K_w$  = water dissociation constant

$P_T$  = total phosphate species concentration (M)

$Q_P$  = pump flow rate (mL/s)

$V_R$  = reactor volume (mL)

$t$  = process time (h)

$t_P$  = cumulative pumping time in eq 15 (s)

$Z_o$  = total concentration of inert species (eq/L)

$\alpha_0, \alpha_1, \alpha_2$  = fractions of the total inorganic carbon species that are present as  $\text{CO}_2^*$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ , respectively.

$\alpha_{P1}, \alpha_{P2}, \alpha_{P3}$  = fractions of the total phosphates species that are present as  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ , respectively

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