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Saturated pH and Total Inorganic Carbon from CO_2 Solubility Related to Algal Growth

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Abstract: Solubility of CO_2 in media formed one-or-more of four forms of inorganic carbon species: carbonic acid, aqueous carbon dioxide, bicarbonate, and carbonate and generated hydrogen ion affecting the medium pH. The saturated TIC and pH were studied using RO water, RO+, GM and GM+ with air (0.038%), 0.5%, 1.0%, 1.5%, 2.0% and 10% CO_2 under atmospheric pressure at temperatures of 25, 35, 45, and 55˚C. Chemical species existing in the media formed additional inorganic carbon species functioning as a buffer, resulting in raising the medium pH. The NaOH boosted the TIC holding capacity of the media and improved the saturated pH. At a specific CO_2-enriched air and medium, the saturated pH linearly increased with respect to increased temperature, which implied the decreasing of TIC. However, the saturated TIC concentration nonlinearly decreased with respect to temperature. At a specific medium and temperature, the saturated pH nonlinearly decreased with respect to increased CO_2 concentration whereas the TIC concentration linearly increased with respect to increased CO_2-enriched air. At a specific CO_2-enriched air, medium and temperature, increasing of TIC concentration decreased the medium pH. The saturated TIC and pH became stable at a same period of time; however, the correlation of the TIC and pH was invalid. The saturated pH can be used to specify the saturation condition of TIC.

Keywords: Solubility of CO_2, Total inorganic carbon, saturated pH, Algal Growth

I. INTRODUCTION

This study is to investigate changes in pH of defined media corresponding to changes in total inorganic carbon (TIC) concentration during the CO_2 mass transfer from the absorption of gaseous CO_2. The fraction of TIC depends on the equilibrium pH. CO_2 dissolves into ground water or media in a series of chemical reaction and becomes aqueous CO_2, carbonic acid, bicarbonate and carbonate as shown in Equations (1) - (4).

During this process, not only is inorganic carbon formed, but also free hydrogen ions, which decrease media pH. This can be simply calculated using $pH = -\log_{10}\left[H^+\right]$, where $[H^+]$ is a molarity of the hydrogen ion. The simple formula for pH calculation becomes very complex when the media consists of several chemical species at a wide range of temperatures, pressures and CO_2 concentrations.

$$CO_2(g) \leftrightarrow CO_2(aq) \quad (1)$$
$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq) \quad (2)$$
$$H_2CO_3^*(aq) \leftrightarrow HCO_3^- + H^+ \quad (3)$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (4)$$

The distribution of these inorganic carbon species is pH-dependent as shown in Fig.1, where that aqueous CO_2 ($H_2CO_3^*$) predominates when the pH falls below 6.3, HCO_3^- predominates at pH values between 6.3 and 10.3, and CO_3^{2-} is the major species at pH values above 10.3 [1-4].

Media pH is an important factor that could identify availability of inorganic carbon species for an aquatic photosynthetic organism and is one of crucial parameters influencing growth of algae [4-12]. According to Bano and Siddiqui, cyanobacterial species preferred to grow near neutral to alkaline pH and have growth optimum at near neutral [13-14].

Yet, there are numerous exceptions. Several studies have reported that many extremophiles can adapt to grow best at extreme pH; for example, cyanobacteria, Oscillatoria/Limnothrix and Spirulina sp. could tolerate on acidic environments of pH 2.9 [15]. In contrast, 13 alkaliplilic cyanobacteria were reported to grow under alkaline conditions, but could not grow well under a neutral-pH condition [16].
Maintaining proper media pH is useful to help specific strains of algae to receive the desired inorganic carbon species and to ensure that the most favored inorganic carbon species for their carbon concentration mechanism are sufficient.

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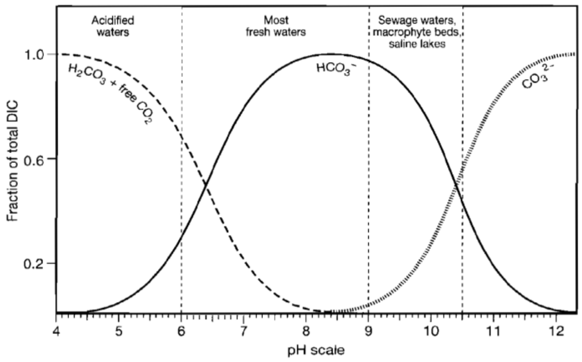

Fig.1. Distribution of inorganic carbon forms in rivers and lakes with respect to changes in pH [1]

Therefore, correlation of the media pH to TIC concentration using experimental and computational calculations could be a very useful tool in predicting photosynthetic behavior by understanding TIC concentration and speciation.

II. PH MEASUREMENT

Media pH, CO_2-enriched air concentrations and temperature were recorded using the Campbell scientific CR1000 data acquisition system as described in experimental setup [17] for reverse osmosis (RO) water and growth media (GM), RO with 3 mM NaOH (RO+) and GM with 3 mM NaOH (GM+) at temperatures of 25, 35, 45, and 55˚C and gas phase CO_2 concentrations of air (380 ppm), 0.5%, 1.0%, 1.5%, 2% and 10.0%.

In addition, 0.1% CO_2 concentration was used to investigate pH changes in GM+. During the CO_2 mass transfer, TIC concentration was measured approximately every six minutes using an OI TOC analyzer in a continuous mode. Media pH was recorded during the same time period as TIC sampling for direct comparison.

A Thermo Scientific submersible automated temperature compensated pH probe and its display and read out accessory, Model alpha pH500 2-Wire pH/ORT transmitter pH/mV/°C, was used to monitor the media pH. The alpha pH500 displays pH from 0.00 to 14.00 with resolution and accuracy of 0.01 pH and ±0.01 pH, respectively.

The submersible pH probe is appropriate for a temperature range from -10.0 to 110.0˚C with resolution and accuracy of 0.1 ˚C and ±0.5˚C, respectively. The output of the display and read out was connected to the Campbell scientific CR1000 data acquisition and programmed to the data acquisition system. Temperature, pH, and gas phase CO_2 concentrations were recorded every minute.

An air flow rate of approximately 18.7 LPM was blended with CO_2 to achieve the desired CO_2 concentration. Bubbling of this mixture into a 3L Erlenmeyer flask was initiated after the data acquisition system was activated.

III. EXPERIMENTAL RESULTS

A. TIC Concentration and Media pH as a function of Time

Fig. 2 plots TIC concentration as a function of time until saturation for each temperature tested for a gas phase CO_2 level of 0.1% in growth media plus 3mM of NaOH (GM+). Fig. 3 plots the media pH over the same time interval as TIC concentration measurements in Fig. 2. The data in Figs. 2 and 3 show that increasing TIC concentration decreased the media pH.

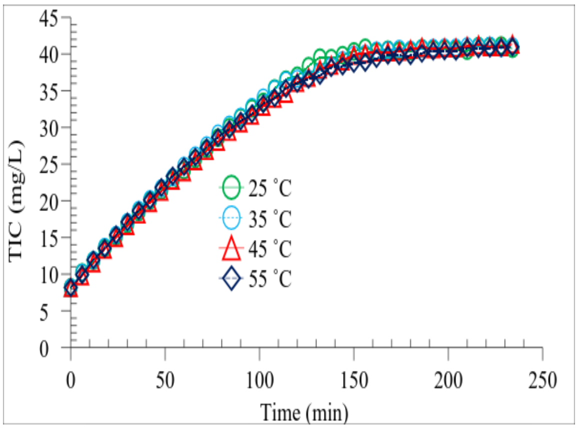

Fig. 2. TIC Concentrations in GM+ with 0.1% CO_2

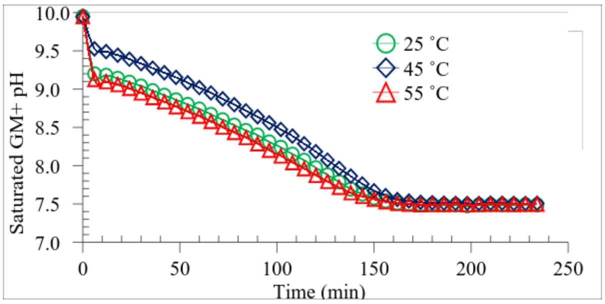

Fig. 3. GM+ pH with 0.1% CO_2

Data shown in Figs. 4 - 7 illustrate the changes in pH and TIC concentrations for two media (GM and GM+) at 25˚C for gas phase CO_2 concentrations of air (380 ppm), 0.5%, 1.0%, 1.5%, 2% and 10.0%.

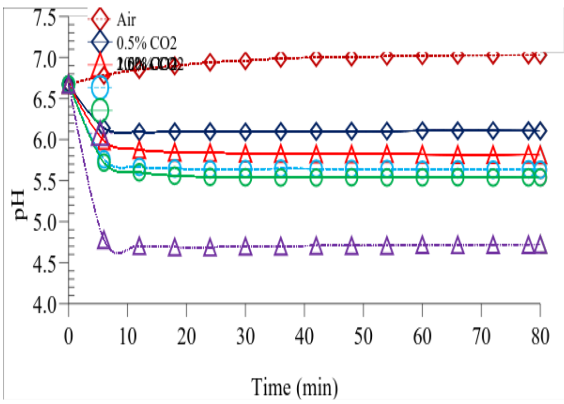

Fig. 4. pH of GM at 25˚C for several gas phase CO_2 concentrations

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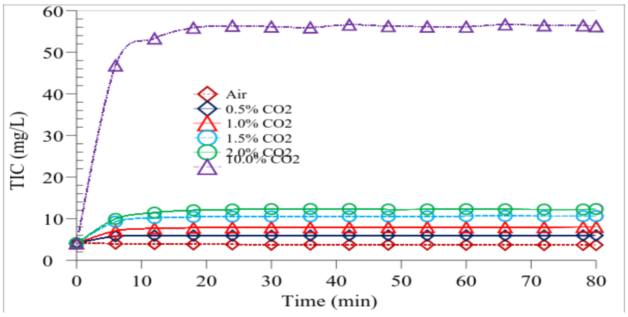

Fig. 5. TIC concentration in GM at 25˚C for several gas phase CO_2 concentrations

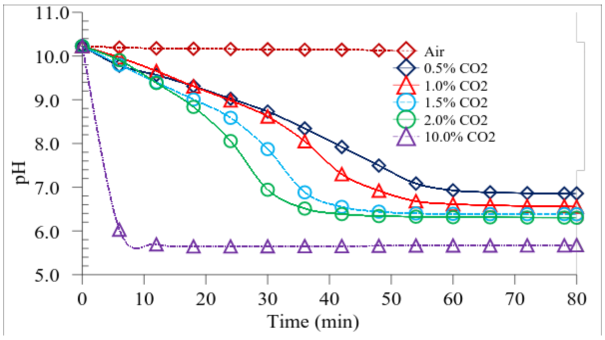

Fig. 6. pH of GM+ at 25˚C for several gas phase CO_2 concentrations

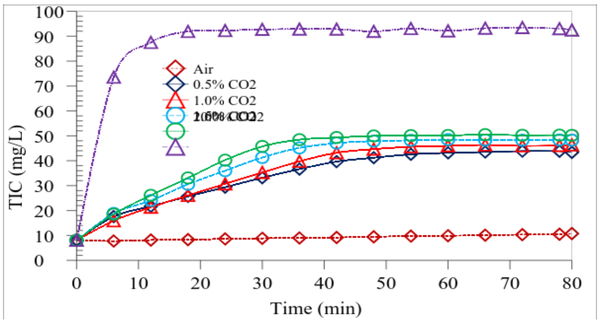

Fig. 7. TIC concentration in GM+ at 25˚C for several gas phase CO_2 concentrations

The results for TIC concentration and pH as a function of time for GM and GM+ media are consistent with the results found with RO water and RO+ media. Specifically, as TIC levels increase, pH decreases. And as TIC levels reach saturation values (or equilibrium), pH tends to reach equilibrium.

B. Determining Saturation pH

The media pH from each experimental condition is shown in Table 1. TIC concentrations were taken from three replicate analysis of each media sample and averaged for each reported value. To determine the saturation value for pH, the last five data points of pH corresponding to the last five values of TIC concentration (used to find TIC saturation) were averaged and reported as the saturation pH for that specific condition. These data were also used to calculate standard deviation (STDEV), coefficient of variance (CV), absolute and relative errors. However, the STDEVs for RO water and GM, and RO+ and GM+ for CO_2 concentrations of 1.5%, 2.0% and 10% were less than 0.008, whereas it was below 0.1 for RO+ and GM+ for air, and 0.5% and 1.0% CO_2. Therefore, only saturated pH in RO water, RO+, GM and GM+ are reported.

Table 1 Saturated media pH

Media pH				T (˚C)	$\%CO_2$
GM+	GM	RO+	RO		
10.11	7.03	10.03	6.02	25	Air
9.82	6.99	9.67	6.20	35	
9.50	7.04	9.35	6.20	45	
9.28	7.09	9.14	6.22	55	
7.49				25	0.1
-				35	
7.51				45	
7.50				55	
6.88	6.11	6.71	5.14	25	0.5
7.03	6.15	6.80	5.28	35	
7.04	6.22	6.90	5.31	45	
7.29	6.23	6.95	5.30	55	
6.58	5.82	6.40	4.88	25	1.0
6.62	5.84	6.48	4.90	35	
6.73	5.86	6.61	4.95	45	
6.87	5.89	6.65	4.96	55	
6.39	5.63	6.24	4.77	25	1.5
6.48	5.66	6.29	4.81	35	
6.61	5.72	6.42	4.88	45	
6.69	5.74	6.50	4.87	55	
6.31	5.54	6.15	4.72	25	2.0
6.34	5.51	6.19	4.65	35	
6.44	5.63	6.26	4.68	45	
6.57	5.60	6.42	4.76	55	
5.67	4.72	5.56	4.21	25	10.0
5.72	4.79	5.58	4.30	35	
5.75	4.81	5.59	4.33	45	
5.82	4.81	5.64	4.26	55	

The data indicated that adding the NaOH solution in the media increased the value of saturation pH especially for RO water compared to RO water without the NaOH solution. The saturation pH and pH difference with and without the NaOH solution are tabulated in Table 2.

Table 2 Saturated media pH difference

pH Difference		CO_2 (%)	T (˚C)
GM & GM+	RO & RO+		
3.08	4.01	Air	25
0.77	1.57	0.5	
0.76	1.52	1.0	
0.76	1.47	1.5	
0.77	1.43	2.0	
0.95	1.35	10	
2.83	3.47	Air	35
0.88	1.52	0.5	
0.78	1.58	1.0	
0.82	1.48	1.5	
0.83	1.54	2.0	
0.93	1.28	10	

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Table 2 (Continued)

pH Difference		CO_2 (%)	T (˚C)
GM & GM+	RO & RO+		
2.46	3.15	Air	45
0.82	1.59	0.5	
0.87	1.66	1.0	
0.89	1.54	1.5	
0.81	1.58	2.0	
0.94	1.26	10	
2.19	2.92	Air	55
1.06	1.65	0.5	
0.98	1.69	1.0	
0.95	1.63	1.5	
0.97	1.66	2.0	
1.01	1.38	10	

C. Saturation pH as a Function of Temperature

Media pH data from Table 1 for GM and GM+ were plotted as a function of temperature in Figs. 8 and 9 for GM and GM+, respectively. The media pH inconsistently increased with respect to increased temperature for all CO_2 concentrations except ambient CO_2 at this temperature range. Gradually increasing the TIC value and decreasing of the media pH for the experiment with ambient air indicated that the system was not at equilibrium. Very dilute CO_2 levels in ambient air resulted in a low pseudo-CO_2 mass transfer coefficient and required a much long period of time to reach equilibrium.

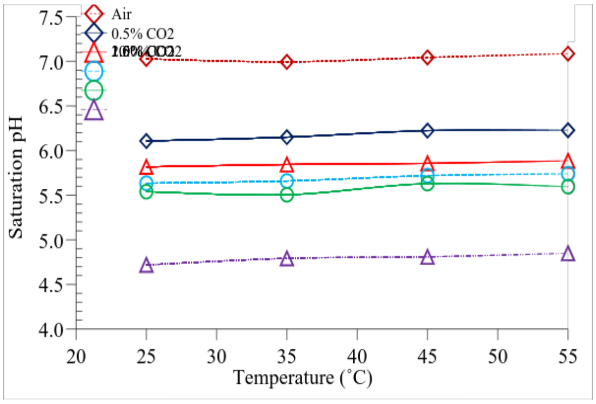

Fig. 8. Saturation pH in GM as a function of temperature

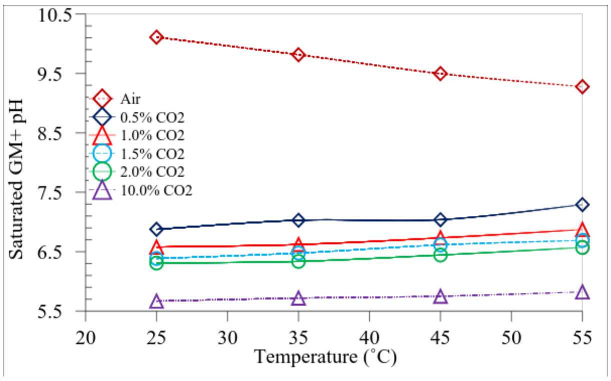

Fig. 9. Saturation pH in GM+ as a function of temperature

D. Saturation pH as a Function of CO_2 Concentration

Data from Table 1 were plotted in Figs. 10 and 11 for RO, RO+, GM and GM+ at 25 and 55˚C for gas phase CO_2 concentrations of 0.5%, 1.0%, 1.5%, and 2%.

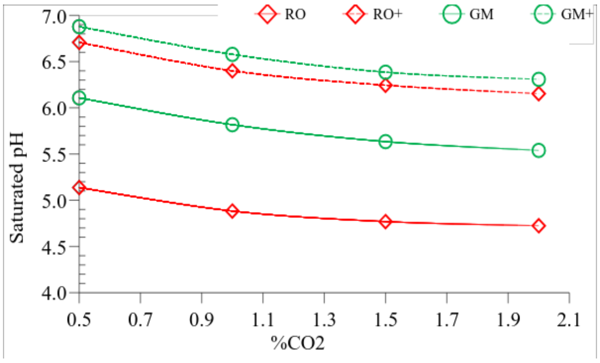

Fig. 10. Saturation pH at 25 ˚C as a function of CO_2 concentration

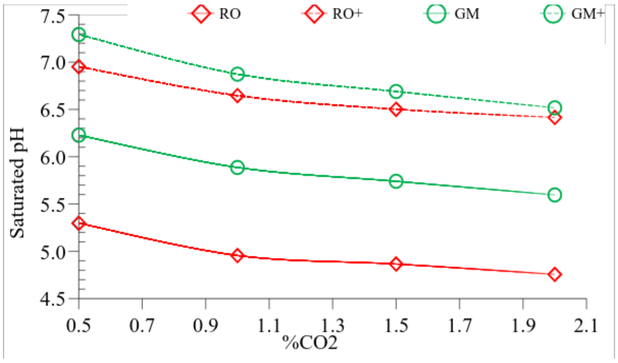

Fig. 11. Saturation pH at 55 ˚C as a function of CO_2 concentration

Saturation pH shown in all cases in Figs. 10 and 11 was nonlinear with respect to change of the gas phase CO_2 concentration. Driving force for CO_2 solubility increased with respect to increased CO_2 concentration; a high CO_2 concentration provided high TIC concentration compared to a low CO_2 concentration. A higher TIC concentration reduced the saturation pH.

IV. CONCLUSION

Media pH inversely followed TIC values for all experimental conditions. However, an exact correlation between decreasing TIC concentration and increasing the media pH is complex to determine because of the combined effects of temperature, CO_2 level, media chemistry and even the accuracy of the pH probe.

However, the trends were observed. Although the TIC concentration nonlinearly decreased with respect to increased temperature, the saturation pH linearly increased. Conversely, as the TIC concentration linearly increased with respect gas phase CO_2 concentration, the saturation pH nonlinearly decreased. The saturation value of TIC and pH were reached at the same time. This indicates that equilibrium pH may be used to specify the saturation condition of TIC. However, the saturation pH with unknown initial pH cannot be used to quantify the amount of TIC concentration especially when the media consists of various chemical species.

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BIOGRAPHY

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