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Efficient storage and utilization of CO_2 in open raceway ponds for cultivation of microalgae

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Abstract−For efficient storage and utilization of CO_2 in open raceway ponds, the effects of cultural and operational parameters were studied. A 10 m^2 indoors raceway pond was operated to determine CO_2 storage capacity, average rate of absorbed CO_2 losses and mass transfer coefficient for CO_2 outgassing from various pH, salinity and alkalinity regimes of culture medium; mixing velocities and culture depths. Average rate of CO_2 outgassing for saltwater (35 ppt salinity) at 40 meq/L alkalinity was 40-fold higher than seawater (35 ppt salinity and 2.3 meq/L alkalinity) at pH 8. Operating at lower pHs or salinities aggravated CO_2 outgassing. An empirical equation for CO_2 outgassing average mass transfer coefficient, $\overline{K}_L$, was developed as a function of mixing velocity and depth. *Nannochloropsis* sp. PTCC6016 was cultivated in the pond for 14 days. Due to higher amount of outgassing, CO_2 utilization efficiency declined as the productivity in the pond decreased.

Keywords: CO_2, Open Raceway Pond, Microalgae, Utilization Efficiency, Outgassing, $\overline{K}_L$

INTRODUCTION

Photosynthetic activity of most microalgal cultivation systems requires dissolved CO_2, essential nutrients dissolved in the liquid medium and light [1-3]. Open ponds are common systems for mass cultivation of microalgae. The pond is designed in a raceway configuration, in which a paddlewheel circulates and mixes the cultivation medium containing algal cells and nutrients at the flow velocity of 15-30 cm/s. The depth of the cultures is generally 10 to 30 cm [4,5].

With a cellular carbon fraction of 0.5 and CO_2 being the only carbon source, a minimum of 1.83 kg CO_2 per kg of biomass must be provided, for oil rich microalgae can go up to 3 kg CO_2 per kg of biomass [1,6,7]. As pure air is not sufficient for CO_2 supply, carbon dioxide-enriched gas mixture should be introduced through the system. The cost of supplying sufficient CO_2 to large-scale cultures of microalgae is a major economic constraint [8,9]. CO_2 has a low solubility in water and unlike other microalgal nutrients must continually be replenished in a large-scale production pond [9].

Efficient delivery, storage and utilization of carbon dioxide in microalgal ponds are significant factors in the economic design of the pond and cultivation of microalgae. While simple design of countercurrent carbonation sumps can provide up to 90% CO_2 injection efficiency [9], maximum storage of CO_2 in the pond and efficient utilization of CO_2 by microalgae are complicated issues in the operation of microalgal open raceway ponds. As the raceway ponds have a large surface area to volume ratio, absorbed CO_2 can easily escape from the culture medium to the atmosphere, while the water tries to equilibrate with lower concentration of CO_2 in the air. The assimilation of CO_2 by rapidly growing algae and outgassing cause reduction in the free CO_2 level in the culture, thereby a disturbance of entire carbonate buffer system and a pH rise in the pond [6,10]. Thus, large-scale algal cultures are subjected to cycles of CO_2 and pH level between recarbonation events. These cycles depend on the pond size, hydrodynamics and the number of carbonation stations. In mass microalgal cultures, the pH of the pond must be maintained in the optimum range for cultivation of the desired species and to prevent the depletion of carbon in the culture medium [10]. Careful system design and operating considerations can reduce the frequency and amplitude of these cycles and, thus, lead to a better utilization of solar energy by microalgae. One problem of open systems is obtaining sufficient carbon storage with minimum amount of CO_2 outgassing. To evaluate the utilization efficiency of injected CO_2 in a pond, the losses of CO_2 must be estimated. Thus, determining the value of mass transfer coefficient for CO_2 outgassing, K_L, is necessary [11,12].

One of the most important aspects in economically viable production of biodiesel or other low value products from microalgae is to minimize the capital and nutrient costs by optimization of engineering and design parameters [4]. Although several published works have been devoted to the phenomenon of gas-liquid CO_2 exchange in different types of microalgal cultivation systems [7,13-15], our study was the first to comprehensively investigate the influence of various operational and cultural parameters on CO_2 outgassing and CO_2 storage capacity of culture medium in raceway pond type cultivation systems. This is a central issue in the operation of microalgal open pond systems as these parameters must be used to optimize for productivity and overall CO_2 utilization efficiency. An em-

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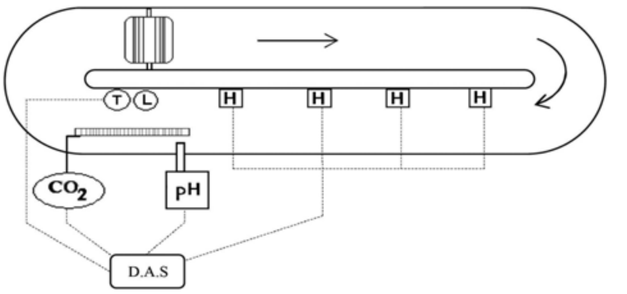

Fig. 1. Schematic view of the 10 m^2 open raceway pond.
H: heater pH: pH sensor
T: temperature sensor CO_2: carbonation station
L: level sensor D.A.S: data acquisition system

pirical correlation has also been developed for K_L, based on data from operation of a raceway pond.

MATERIALS AND METHODS

1. Raceway Pond Design

Experiments were carried out in a 10 m^2 pond of 1.2 m wide and 8.4 m long, divided by a central baffle to form a raceway. To minimize friction at the pond bottom and its effect on outgassing losses of CO_2, as a consequence of change in hydrodynamic of the pond, the pond bottom was lined with polyethylene (PE) (Fig. 1). The pond was operated under sunlight radiation and indoors to exclude the effect of wind speed on CO_2 mass transfer. Required flow velocity was provided by an eight-blade paddle wheel. Data from all probes was captured by a data acquisition system, connected to a computer for on-line monitoring, logging and control.

2. Microorganism and Culture Conditions

The microalga used in the present study was *Nannochloropsis* sp. PTCC6016 with a high growth rate and oil content, isolated previously [16,17] from the Persian Gulf for our large-scale cultivation of microalgae. The required inoculum for cultivation of the strain in the 10 m^2 pond was grown indoors in a one m^2 Plexiglas pond, at pH 7.5 and 20 °C under fluorescent lamp illumination at 200 μmol/m^2/s and using diurnal illumination of 12 h light/12 h dark (L/D) cycles. To prepare the culture medium, the following nutrients were added per liter of artificial seawater: 75 mg $NaNO_3$, 5 mg $NaH_2PO_4 \cdot H_2O$, 4.4 mg $Na_2EDTA \cdot 2H_2O$, 3.2 mg $FeCl_3 \cdot 6H_2O$, 179 μg $MnCl_2 \cdot 4H_2O$, 21.9 μg $ZnSO_4 \cdot 7H_2O$, 9.95 μg $CoCl_2 \cdot 6H_2O$, 9.76 μg $CuSO_4 \cdot 5H_2O$, 6.18 μg $Na_2MoO_4 \cdot 2H_2O$, 100 μg vitamin B1, 0.5 μg Biotin, 0.5 μg vitamin B12 [18].

3. Measurements of Microalgal Productivity and Density

The productivity for the 10 m^2 pond was measured based on biomass dry weight. In every single day of cultivation, four 35 ml samples were collected from various locations of the pond. The samples were centrifuged at 15,000 g, washed with NaCl solution and distilled water to remove non-biological material, dried at 100 °C for 18 hr and weighed. Productivity was measured on a daily basis and reported as g/m^2/d. Cell density was determined using optical density measurements of the absorbance at 590 nm with a spectrophotometer (Unicom UV-Vis spectrometry, China).

4. Measurements of Parameters

The temperature, pH and depth of culture medium were measured by sensors located in the liquid bulk as shown in Fig. 1. These parameters were controlled and monitored using a control system. Several electric heaters were used to maintain temperature for experiments. The salinity and alkalinity were measured by standard methods [19]. These two parameters were changed by addition of sodium chloride and sodium bicarbonate powder in the pond, respectively. $NaHCO_3$ increases the alkalinity level without affecting the pH significantly [20]. Average flow velocity was measured with an open channel flowmeter (Marsh-McBirney, Inc., model-2000, USA). Mapping of velocities has identified the best place for measuring average velocities to be approximately at 10 cm from the pond bottom, exactly before the bend, at the channel in which the paddle wheel was located [21]. At least ten flow velocity measurements were made and the average velocity was calculated. Input gas streams of pure CO_2 were delivered through mass flow controllers (Omega Engineering, Inc., FMA-A2121, USA) and for distribution of fine gas, CO_2 was introduced by means of 1.5 cm diameter and one m long porous diffuser, resting on the pond bottom.

5. Carbon Storage Capacity and Average Rate of Carbon Dioxide Outgassing

By measuring temperature, salinity, pH and alkalinity of liquid phase, dissolved carbon dioxide and total inorganic carbon (TIC) were determined from carbonate equilibrium equations according to previous studies [22-24]. CO_2 storage capacity of the pond was obtained by calculating the change in dissolved carbon dioxide in the liquid phase for the specified pH range of the pond.

For the liquid phase, the rate of CO_2 outgassing from surface of the pond is expressed as follows:

$$R_{CO_2} = K_L(C^*_{CO_2} - C_{CO_2})$$

where R_{CO_2} is the rate of CO_2 outgassing per unit surface area of the pond (mol/m^2/s), K_L denotes the coefficient of mass transfer for CO_2 outgassing (m/s), $C^*_{CO_2}$ denotes equilibrium CO_2 concentration with the air (mol/L) and C_{CO_2} is dissolved CO_2 concentration in the pond (mol/L).

For each condition of parameters, average rate of absorbed CO_2 losses was determined by measuring the decrease in total inorganic carbon per unit time and surface area, after sparging CO_2 in the non-inoculated liquid, traveling between recarbonation events. Three samples were collected for each analysis from the liquid phase mixed gently in front of the paddle wheel. As demonstrated by earlier experiments [25-27], the existence of algae has no significant effect on CO_2 transfer rate of culture medium. pH was monitored over the course of the experiments at 15 min intervals.

6. Determination of Average Surface Mass Transfer Coefficient for CO_2 Outgassing

This experiment was performed by supplying CO_2 into water of fixed alkalinity and allowing the pH to rise as a consequence of CO_2 losses from the surface of the pond. Dissolved CO_2 concentration and decrease of total inorganic carbon concentration were calculated from the observed pH change, using equilibrium constants corrected for temperature and salinity [24,28,29]. The average mass transfer coefficient for CO_2 outgassing was then determined by linear regression of the calculated average CO_2 driving force with the rate of change in total dissolved inorganic carbon per unit surface area of the pond. Henry's law was used to calculate the equilibrium CO_2 level with the air, corrected for temperature and ionic strength [28, 29].

7. CO_2 Injection Efficiency and Utilization Efficiency

The CO_2 injection efficiency was determined as the ratio of the increase in total inorganic carbon level in the liquid phase after injection of CO_2, to the total amount of CO_2 injected into the pond, measured by mass flow controller. The utilization efficiency was estimated by dividing the amount of CO_2 fixed in the biomass by the total CO_2 injected into the pond.

RESULTS AND DISCUSSION

1. CO_2 Storage Capacity of the Pond

As a consequence of CO_2 outgassing and microalgae utilization, CO_2 concentration decreases and pH rises in the pond. Hence, to prevent that variations in CO_2 and pH at critical level limit the photosynthesis, a carbonation cycle is devised in the pond. In this cycle the culture medium travels from carbonation station after a specified period of time. In the flow of raceway ponds, adequate amounts of CO_2 must be injected into the carbonation stations, and subsequently be stored in water to meet the carbon demand of microalgae and compensate any outgassing of CO_2, as the water travels between recarbonations (resupply events). In an optimized cultivation system, CO_2 content in the medium before reaching the carbonation station should not be lower than the critical amount of CO_2 required for unlimited photosynthesis [6,11,31]. Depending on the size of the pond, this injection can be continuous (sizes more than 0.5 hectare) or intermittent, with one or more carbonation systems along the pond [6].

Table 1 presents the calculated carbon storage capacity at different alkalinities and depths of two water resources with different ionic strengths. The pH in the water resources was considered to range within 6.5 to 8.7, which is the common pH range for outdoor cultivation of most microalgae [6,9]. The results show that the amount of CO_2 stored in the pond for fixed pH range of operation is directly proportional to alkalinity and depth of water in the pond. Table 1 also indicates that CO_2 storage capacity of high salinity waters is less than that of freshwater due to its effects on carbonate equilibrium constants.

The duration of carbonation required to decrease pH from 8.7 at different alkalinities and salinities of water resources was measured,

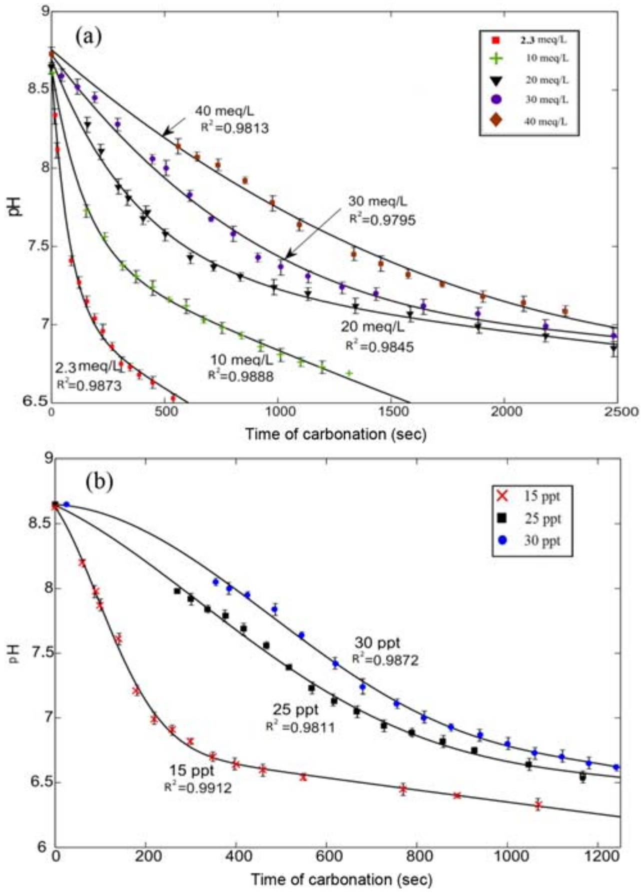

Fig. 2. Duration of carbonation required to introduce CO_2 (at 25 slpm) into the 10 m^2 raceway pond of 20 cm depth by carbonation system, at different alkalinity of freshwater (a) and at different salinity of liquid phase (2.3 meq/L alkalinity) (b).

as CO_2 was introduced through mass flow controller at 25 slpm (standard liters per minute) flow rate to the 10 m^2 pond at 20 cm depth (Fig. 2(a) and 2(b)). Injection efficiency of carbonation system was 57-69%, depending on the alkalinity of the liquid phase. Liquid height and gas flow rate had no significant effect on injection efficiency [9]. The measurements were done after a short period of paddle wheel

Table 1. Carbon storage capacity and duration of carbonation required to introduce CO_2 (at 25 slpm), for the 10 m^2 pond at various alkalinities, depths and salinities during pH change from 8.7 to 6.5 and 57-69% carbonation injection efficiency

		Freshwater (salinity=0 ppt)		Saltwater (salinity=35 ppt)	
Alkalinity (meq/L)	Depth (cm)	Carbon storage capacity (mol/m^2)	Time of carbonation (s)	Carbon storage capacity (mol/m^2)	Time of carbonation (s)
2.3	15	0.03	165	0.0591	85
	20	0.04	215	0.0788	110
	25	0.05	270	0.0985	135
10	15	0.1503	540	0.2955	275
	20	0.2004	720	0.3940	365
	25	0.2505	900	0.4925	460
30	15	0.4510	1440	0.8866	735
	20	0.6013	1920	1.1821	975
	25	0.7516	2400	1.4776	1220

mixing.

The duration of carbonation did not show any significant difference at various mixing velocities in the range of 15 cm/s to 35 cm/s. For example, it took 910 seconds for pH to change from 8.7 to 7, for freshwater at 30 meq/L alkalinity and 20 cm depth in a pond with 15 cm/s mixing velocity, and 890 seconds for the same condition in a pond with 35 cm/s mixing velocity. The results show that at high alkalinity levels, large amounts of CO_2 must be injected so that a small change in pH can be observed. When the carbon dioxide is dissolved in the liquid phase, it is stored in the inorganic carbon pool in three forms of H_2CO_3 (CO_2), HCO_3^- and CO_3^{2-}, depending on pH of liquid phase (Fig. 3). It is evident from Figs. 2(a) and 2(b) that the required time for carbonation increases significantly at lower operating pHs. In the narrower operating pH range the pond shows less CO_2 storage capacity; therefore, to maintain the level of productivity, the number of carbonation stations (for large ponds) must be increased, which corresponds to a decreased time between recarbonation events (for small ponds).

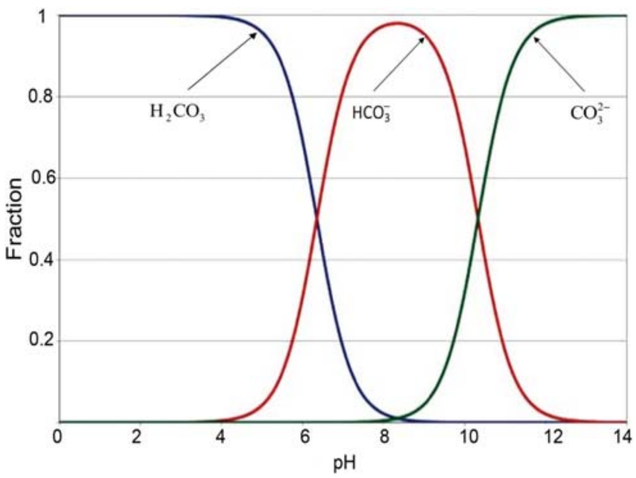

Fig. 3. Relative fraction of H_2CO_3 (CO_2), HCO_3^- and CO_3^{2-} in a liquid phase at 35 ppt salinity and 2.3 meq/L alkalinity as a function of pH [6].

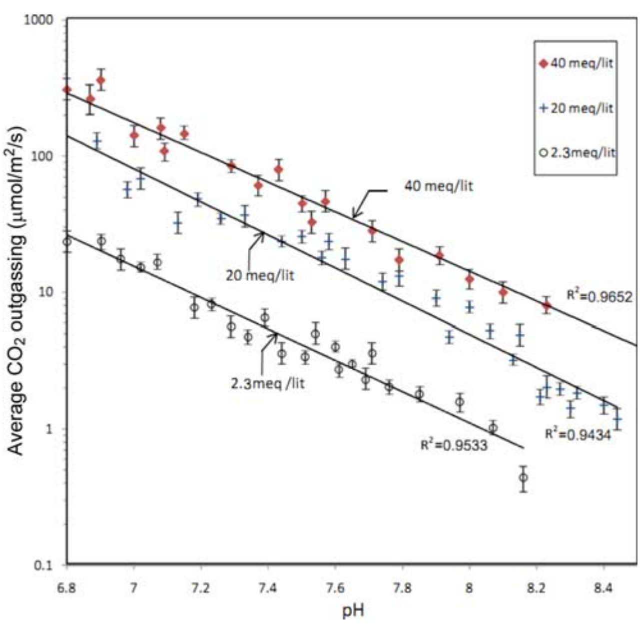

Fig. 4. Rate of CO_2 outgassing during operation of the 10 m² pond at various alkalinities of saltwater (35 ppt salinity). In each case, pond depth and mixing velocity are 20 cm and 25 cm/s, respectively.

2. Average Rate of Absorbed CO_2 Outgassing

The average rate of absorbed CO_2 outgassing was determined experimentally for the 10 m² pond at 25 cm/s average mixing velocity, 20 cm depth and constant 20 °C temperature. The results of CO_2 outgassing rate are shown in Fig. 4 at different alkalinities of saltwater as pH change in the pond. The average rate of absorbed CO_2 losses increased at higher alkalinities. Due to larger total carbon storage capacity in a liquid phase with higher alkalinity (Table 1), the driving force for outgassing increases. Outgassing for saltwater with 35 ppt salinity and 40 meq/L alkalinity was 40-fold higher than seawater with the same salinity and 2.3 meq/L alkalinity at pH=8, but, it took more time for pH to change in the pond with higher alkalinity. For example, it took 450 min at 40 meq/L alkalinity and 250 min at 2.3 meq/L alkalinity for pH to change from 7 to 8 (Fig. 5).

As shown in Fig. 4, average rate of absorbed CO_2 losses increased at lower pHs, which is critical in particular at high alkalinity levels. At lower pHs, dissolved CO_2 concentration and consequently driving force for outgassing increased. Outgassing steeply increased below pH 8 for seawater at 35 ppt salinity and 2.3 meq/L alkalinity. This loss can be minimized by maintaining pH at higher levels. Thus, to minimize CO_2 losses from the pond without a significant productivity reduction, it is favorable in open ponds to have a low alkalinity when the desired species require a low pH for optimal growth and a high pH if the medium has a high alkalinity. The upper limit of operating pH range in a raceway pond is set by the growth and productivity response of the algae to high pHs as well as low CO_2 concentrations and calcium carbonate precipitation [32]. The latter is especially acute when the alkalinity is low, as in the seawater (10.3 mM Ca^{+2} concentration and 2.3 meq/L alkalinity). This precipitation results in low carbon storage capacity, due to loss of alkalinity. In seawater, $CaCO_3$ is precipitated considerably at pHs

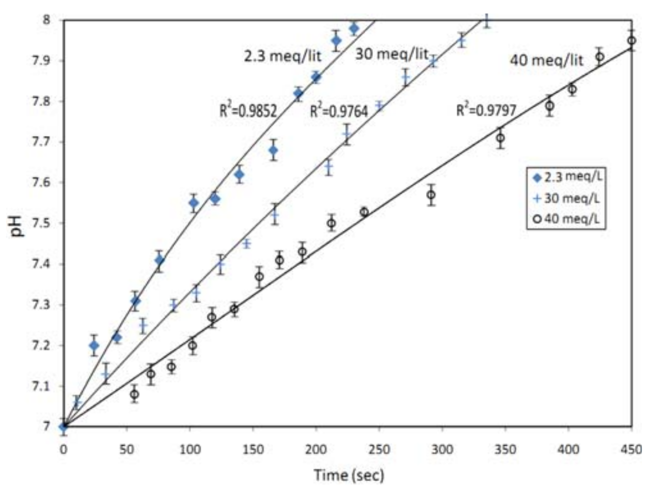

Fig. 5. Time dependent variation of pH in the 10 m² pond due to CO_2 outgassing, at different alkalinities of saltwater at 35 ppt salinity. In each case, pond depth and mixing velocity are 20 cm and 25 cm/s, respectively.

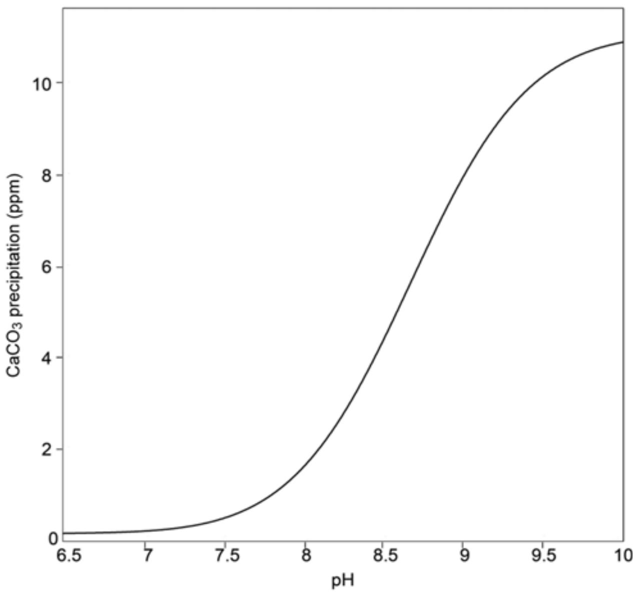

Fig. 6. $CaCO_3$ precipitation at various pH of seawater [32].

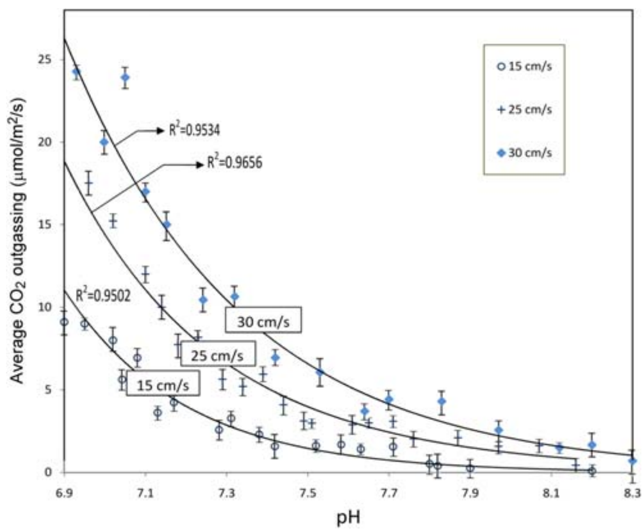

Fig. 8. Effects of mixing velocity in the pond at 20 cm depth on the CO_2 outgassing rate of liquid phase at 2.3 meq/L alkalinity and 35 ppt salinity.

above 8 (Fig. 6). In the high alkalinity cases, growth and productivity response of microalgae dictate the upper limit of pH. The effects of low CO_2 concentration (25 μM) and high pH (9-10) (the economic conditions for operation of open ponds), on productivity of several species has been investigated [9]. At low CO_2 concentration and high pH cultures, the productivity was 10-15% lower than in control cultures, which is not significant in a practical sense.

CO_2 outgassing was determined for different ionic strengths of liquid phase (Fig. 7). As a consequence of the effects of ionic strength on the carbonate equilibrium constants and the amount of carbon storage capacity, CO_2 outgassing was higher in freshwater mediums than in saltwater ones.

The results (Fig. 8) show that doubling mixing velocity elevates the average rate of absorbed CO_2 outgassing about 1.5 times due to the higher rate of surface renewal and hence mass transfer coefficient for outgassing. On the other hand, for large-scale cultivation systems, increase in mixing velocity can decrease the time intervals between recarbonations and subsequently pH range experienced in the pond. Therefore, mixing velocity must be optimized for these two conflicting effects. Decreases in volume of liquid per unit surface area acted to aggravate CO_2 outgassing and decreased carbon storage capacity (Fig. 9 and Table 1). Hence, the depth of liquid must be increased up to the extent that not to limit productivity due to reduction in light availability for photosynthesis.

To determine the pond size with fixed number of carbonation stations, the number of carbonation stations required (or the frequency of carbonation in small ponds) and the CO_2 transfer stations

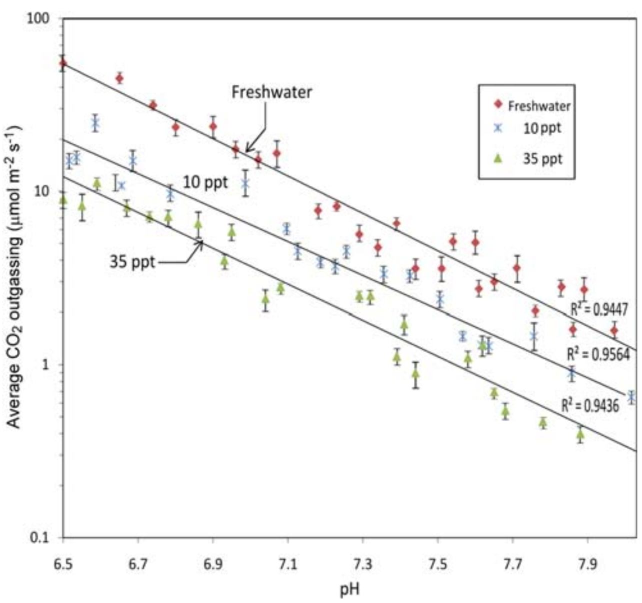

Fig. 7. Rate of CO_2 losses during operation of the 10 m^2 raceway pond at various salinities of liquid phase. For each case, pond depth, mixing velocity and alkalinity are 20 cm, 25 cm/s and 2.3 meq/L, respectively.

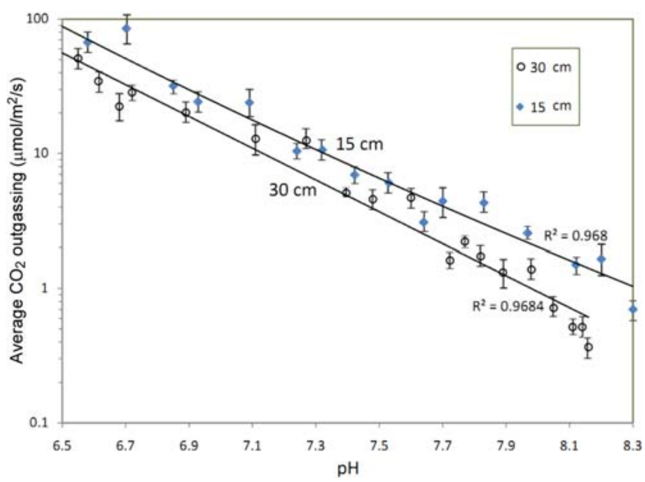

Fig. 9. Rate of CO_2 outgassing from the 10 m^2 pond at two different depths of liquid phase (35 ppt salinity and 2.3 alkalinity), 15 cm and 30 cm, and 25 cm/s mixing velocities.

spacing, first, the optimized pH range experienced in the pond should be specified with the consideration of CO_2 outgassing and productivity. pH range, depth and alkalinity will determine the total carbon storage capacity of the pond. As the required CO_2 for photosynthesis and outgassing in distance between carbonation stations must be equal to (or exceed) that stored in the pond in this distance, an adequate frequency of recarbonation should be determined. The frequency and the optimized mixing velocity values are used to determine the distance between carbonation stations, and thereby the pond size.

3. Average Mass Transfer Coefficient for Absorbed CO_2 Outgassing

Experimental and theoretical correlations developed for outgassing mass transfer coefficient of CO_2, K_L, for lakes, estuaries [33, 34], aquaculture ponds [35] and open ponds with different configurations [36,37] are not suitable for open raceway ponds, where irregular surface deformations occur due to its special design. They provide only approximate estimate for K_L; therefore, the accurate amount must be derived empirically from prototypes and pilots.

Table 2. Mass transfer coefficient for CO_2 outgassing, K_L, at different average linear velocities and depths of culture medium in the 10 m^2 raceway pond

Depth (cm)	Velocity (cm/s)	K_L (m/s)
15	15	1.43×10^{-5} (R^2=0.963)*
	25	2.6×10^{-5} (R^2=0.942)
	30	3.31×10^{-5} (R^2=0.955)
20	15	1.28×10^{-5} (R^2=0.932)
	25	2.3×10^{-5} (R^2=0.966)
	30	2.8×10^{-5} (R^2=0.953)
25	15	1.1×10^{-5} (R^2=0.971)
	25	2×10^{-5} (R^2=0.944)
	30	2.5×10^{-5} (R^2=0.955)

*Coefficient of determination (R^2)

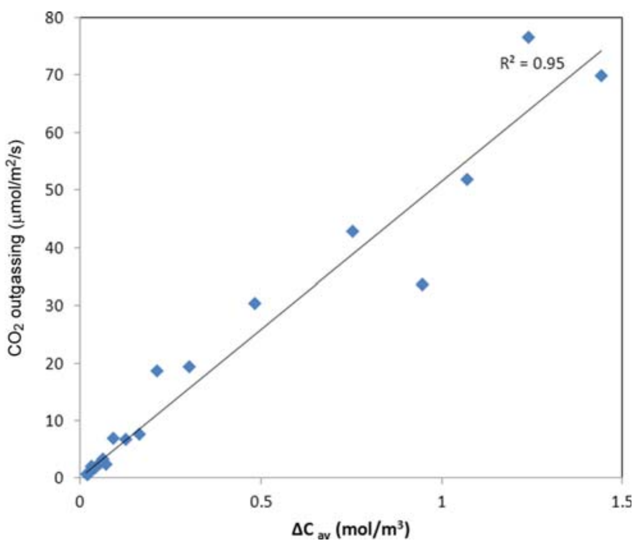

Fig. 10. Rate of CO_2 outgassing vs. average CO_2 driving force, for operation of the 10 m^2 pond at an average mixing velocity of 30 cm/s and 20 cm depth. The slope of the line corresponds to a K_L value of 2.5×10^{-5} m/s.

Mass transfer coefficient for CO_2 outgassing mainly depends on hydrodynamics of the pond [36,37]. It was determined for common operational velocity range (15-35 cm/s) and depth range (10-30 cm) in open raceway ponds for cultivation of microalgae (Table 2). Fig. 10 shows an example of experimental data and fitted line used for determining $\overline{K}_L$ at 30 cm/s mixing velocity and 20 cm depth. The following empirical equation was obtained from a regression analysis:

$$\overline{K}_L=2.79\times10^{-6}\, d^{-0.46}\, v^{1.09} \qquad R^2=0.93$$

where $\overline{K}_L$ is average mass transfer coefficient for absorbed CO_2 outgassing (m/s), d is the height of medium in the pond (cm) and v is the mixing velocity (cm/s). In the range of pH 6.5 to 8.7, the mass transfer coefficient did not vary. Benemann et al. [37] measured the same $\overline{K}_L$ value of 3.4×10^{-5} m/s for a 1.2 m^2 pond at 15 cm depth and 30 cm/s velocity over two pH ranges 6.77 to 7.09 and 7.17 to 7.59. In an alkaline medium, CO_2 is present in an uncatalyzed reaction path, i.e., hydration of CO_2 and subsequent acid-base reaction to form carbonate ion.

$$CO_2+H_2O \longleftrightarrow H_2CO_3 \xleftrightarrow{Instant} 2H^{+}+CO_3^{2-}$$

For common operational pH and alkalinity range in microalgal ponds, the effect of this reaction on CO_2 transfer coefficient is negligible compared with hydrodynamic effects [38]. We measured the same K_L value, even for alkalinities of up to 30 meq/L.

4. CO_2 Utilization in Large-scale Cultivated Open Raceway Pond

To evaluate the utilization of CO_2 in a production pond, strain *Nannochloropsis* sp. PTCC6016 was cultivated in the 10 m^2 raceway pond for 14 days [17]. The pond was operated at 30 cm/s mixing velocity and 20 cm depth. Variation of cell density in the production pond is illustrated in Fig. 11. A portion of stored CO_2 in the pond for an operating pH range, fixed in the biomass and the remaining outgassed during travelling of liquid phase in the pond. For each microalgal productivity in the pond, the mass of carbon fixed in the biomass during the cultivation period was estimated to be 1.83-fold of the biomass produced (dry weight) [1,6] and subsequently, CO_2 lost to the atmosphere through outgassing was esti-

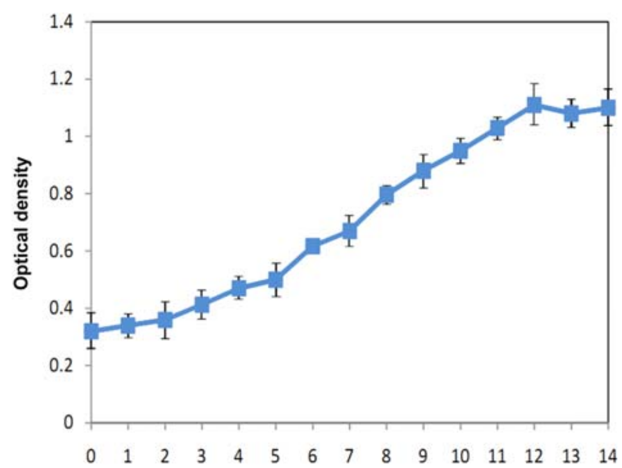

Fig. 11. Cell density in the 10 m^2 pond during 14 day cultivation for *Nannochloropsis* sp.

Table 3. Carbon utilization efficiency in the production pond, at operating pH range of 6.5 to 8.26, 2.3 meq/L alkalinity and 35 ppt salinity of culture medium

Day of cultivation	Productivity[a] ($g/m^2/d$)	Biomass (g/m^2)	Outgassed (g/m^2)	Utilization efficiency (%)
2	4.7	4.22	5.04	31
7	20.4	6.84	2.42	49
9	17.5	6.45	2.81	46
12	8.5	5.49	3.77	39

[a]Based on constant productivity over 10 hr day

mated from a preliminary mass balance for CO_2. The results are shown in Table 3 for operating pH range of 6.5 to 8.26 at 2.3 meq/L alkalinity and 35 ppt salinity of culture medium. At the pH 8.26, there is no driving force for outgassing, but pH of culture media could rise to 10 as a result of CO_2 utilization by microalgae. The data is based on the assumption that the productivity is constant during 10-hr-daylight period. The samples for productivity analysis were taken in the morning and the evening, so no nightly respiration occurred in between. The amount of CO_2 outgassed increased as the pond was operated at lower productivities, and, as a consequence, CO_2 utilization efficiency declined. At the productivity of 20.4 $g/m^2/d$, 26% of the CO_2 absorbed in the pond was lost to the atmosphere through the pond surface. Operation of the pond at the lower productivity 4.7 $g/m^2/d$ increased CO_2 losses to more than 54%. At the maximum productivity of 20.4 $g/m^2/d$, the low CO_2 utilization efficiency, 49%, was mainly caused by low injection efficiency of carbonation system, 57%. In this case, selection of a carbonation system with 95% injection efficiency [9] could increase CO_2 utilization efficiency in the pond up to 70%. Each condition of the parameters in the pond reducing CO_2 outgassing rate can increase CO_2 utilization efficiency.

CONCLUSION

The influence of various operational and cultural parameters on an optimized storage and utilization of CO_2 in open raceway ponds was investigated. For economic CO_2 supply into the pond, especially to produce low value products, design parameters should be selected accurately.

CO_2 outgassing from the pond increased as the pond was operated at lower pHs (especially less than 8 for seawater at 2.3 meq/L alkalinity and 35 ppt salinity), and higher alkalinities, the conditions at which the carbon storage capacity of the pond was increased. Because the pond should have a large carbon storage capacity, and on the other hand, CO_2 outgassing must be minimized, an optimized value of pH and alkalinity for operation of the pond must be selected. In the higher alkalinity cases, more time for CO_2 injection was required to adjust the pH of the pond. Furthermore; it took more time for pH to increase as the pond was operated at the higher alkalinities. CO_2 outgassing was 4.5-fold higher in freshwater at 2.3 meq/L alkalinity than in seawater at the same alkalinity and 35 ppt salinity at pH=7. An empirical correlation for $\overline{K}_L$ was developed, where $\overline{K}_L$ is a function of depth and mixing velocity. Variation of mixing velocity had more effect on the rate of outgassing than the height of medium in the pond. Evaluation of a production pond for cultivation of *Nannochloropsis* sp. showed that higher productivity in the pond results in more efficient utilization of CO_2, due to lower amount of CO_2 outgassing from the pond. At maximum productivity in the pond, low CO_2 utilization efficiency (49%) was mainly due to low injection efficiency (57%).

Accurate setting of the mentioned parameters is important, as they determine the pond size and the number of carbonation stations for cultivation of known species, and as a result, capital costs for carbonators. Another aspect in efficient carbonation of large-scale raceway ponds is to select the best engineering design for supply and transfer systems, in order to maximize injection efficiency, which is the topic of ongoing research.

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