CHAPTER IV

Results and Discussion

4.1 Maximising CO_2 dissolution in bubble column

4.1.1 Effect of pH on total inorganic carbon dissolved in the water

pH in the range of 6 to 10 were chosen to study its effect on CO_2 dissolution in the water because bicarbonate species can be found in this range as dissolved inorganic carbon and, in many cases, suits to be fed into cultivation systems as inorganic carbon source for microalgal growth. Figure 4.1.1 illustrates the time profiles of Total Inorganic Carbon (TIC) measured from TOC analyser in the unit of milligram per litre ($mg \cdot L^{-1}$) at all pH range. During the course of the experiment (from 0 to 60 minutes), the total dissolved inorganic carbon increased steadily with time and accumulated in the bubble column. The maximum dissolution at pH 10 (measured from the total inorganic carbon) was most of the time higher than those obtained at pH 6 and 8. In fact, pH 6 saw the lowest trend of CO_2 dissolution.

From Table 4.1.1, CO_2 dissolution efficiencies (proportion of CO_2 dissolved as TIC in mg divided by the total amount of CO_2 entering the reactor in mg) achieved the highest and lowest at pH 10 and 6, respectively. At the beginning of the experiment, inorganic carbon was able to dissolve quite rapidly in the liquid, but the dissolving rate decreased subsequently. The highest efficiency of 49.81% was obtained at the beginning of experiment with pH 10 (15th minutes). The high efficiency at early stage could be due to the high concentration difference driving force (ΔC) as described in the following mass transfer rate equation:

$$N = kA\triangle C \qquad (4.1)$$

where N = Mass transfer rate ($g \cdot min^{-1}$)

k = Mass transfer coefficient ($m \cdot min^{-1}$)

A = Mass transfer area (m^2)

$\triangle C$ = Concentration difference ($g \cdot m^{-3}$)

(Note: $\triangle C$ = Equilibrium liquid phase concentration ($\overline{Cg}$) – Liquid phase concentration (C_l) where $\overline{Cg}$ is assumed to be the liquid phase concentration which is in equilibrium with gas phase concentration (C_g)).

At the beginning, the concentration of inorganic carbon in liquid was very low compared with the equilibrium concentration ($\overline{Cg} >> C_l$). As the result, high mass transfer rate was observed and this is reflected in the apparent high %efficiency of CO_2 dissolution. At later stage, the dissolved CO_2 (C_l) became high, lowering the concentration difference ($\triangle C$), and so did the mass transfer rate. At sufficient contacting time, C_l reaches approximately the equilibrium liquid phase concentration ($\overline{Cg}$) resulting in $\triangle C \rightarrow 0$ and no further net mass transfer would take place. Fortunately, CO_2 could undergo chemical transformation to bicarbonate and carbonate according to Equation (4.2) and therefore this maintained the liquid phase CO_2 concentration at a lower level than the equilibrium concentration. Consequently, the gas-liquid mass transfer could continue according to the level of ΔC driving force at that particular moment.

The change in pH could manipulate the rate at which CO_2 transforms to bicarbonate and carbonate. Experiment demonstrates that at high pH, this transformation occurred at a more rapid rate. In other words, high pH level or high degree of alkalinity leads to the forward reactions (2) and (3) in Equation (4.2). As the result, a low ΔC for CO_2 could be maintained at a longer period and a high level of CO_2 dissolution could consequently be obtained. It was demonstrated in this section that an increase in pH could lead to a greater dissolution of CO_2 resulting in a greater TIC concentration trend. Within the range of pH investigated, pH 10 gave the highest fraction of inorganic carbon being dissolved in the liquid compared with other pH levels.

$$CO_2\,(g) \xleftrightarrow[(1)]{\qquad} CO_2\,(l) \xleftrightarrow[(2)]{\qquad} HCO_3^- \xleftrightarrow[(3)]{\qquad} CO_3^{2-} \quad (4.2)$$

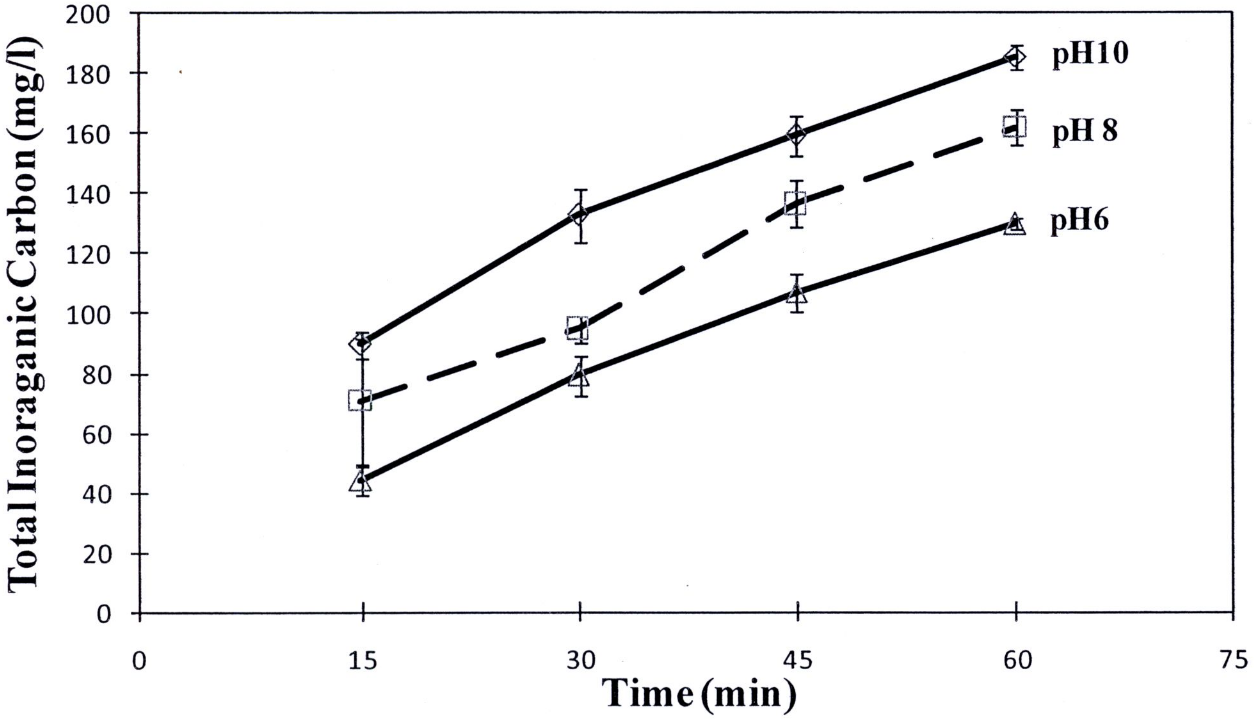


Figure 4.1.1 Total Inorganic Carbon time profile at various pH levels

Table 4.1.1 % Efficiency of CO_2 dissolution at various pH levels

Time (min)	%Efficiency (Carbon Balance)		
	pH 6	pH 8	pH 10
15	22.26	35.83	45.28
30	20.00	23.92	33.41
45	17.98	22.91	26.76
60	16.35	20.42	23.38

4.1.2 Effect of gas-liquid contacting area on total inorganic carbon dissolved in the water

In this section, packing material was fully packed in 1 m high bubble column to enhance the contacting area between gas and liquid. Although the effect of pH on TIC dissolved in the water was already reported in the previous section, the different configurated columns were operated at the various pH levels (at 6, 8 and 10) to ensure that there is no relationship between the two effects. In addition, samples were collected at different heights, at the middle and top of the column. Distinctly, TIC time profile in Figure 4.1.2.1(a) representing the concentration at the top part of the column displayed the highest TIC trend at pH 10. In contrast, pH 6 showed the lowest TIC trend compared with the others which confirms the effect of pH as discussed earlier. Similarly, the highest TIC as shown in Figure 4.1.2.1(b) was achieved at pH 10. Note that there were not much differences between the results at pH 6 and pH 8, and from hereafter, only the results at pH 10 will be discussed unless otherwise mentioned. The highest efficiency, 51.87% at pH 10, was reported at middle of the column as reported in Table 4.1.2. %Efficiency largely decreased with time, e.g. 51.87% at 15th min and then, 35.33% at 30th min because of lower mass transfer rate due to the increase of C_l over time as described in previous section. At the beginning of experiment, at lower position of column, equilibrium liquid phase concentration ($\overline{Cg}$) was largely higher than concentration in liquid (C_l) which resulted in higher %efficiency in CO_2 dissolution at the middle compared with at the top of the column. At a longer time period (30th min and later), not much differences in %efficiency at the top compared with the middle were observed because the influential factor in concentration difference decreased with time.

The effect of gas-liquid on TIC dissolved at pH 10 in different contactor configurations, i.e. bubble and packed column, is illustrated in Figure 4.1.2.2. Adding gas-liquid contacting area (by introducing the packing material) led to a higher rate of CO_2 dissolved in the water. Gas hold up (ε_g) is calculated by the following equation:

$$\varepsilon_g = \frac{V_g}{V} \tag{4.3}$$

where ε_g = Gas holdup
V_g = Volume of gas in the column (L)
V = Volume of liquid in the column (L)

$\varepsilon_{g,b}$ and $\varepsilon_{g,p}$ are equal to 1.1 and 2.3 for the 1m high bubble column and 1 m high packed column, respectively (see Appendix C.2). This means that, provided that the bubble size remained unaltered, using packing material could enhance the gas holdup significantly and this led to a higher contacting area. Proportionally, having a 2 times higher gas holdup, the contacting area was expected to also be two times higher in the packed column than in the bubble column. However, the mass transfer rate does not seem to follow this trend. Dissolution efficiencies of the two systems at pH 10 at 60 min are 23.38% for bubble column and 29.76% for packed column (both at top of the column) (Table 4.1.1). Similarly, at 15th min, 45.28% for bubble column (Table 4.1.1) and 51.81% for packed column (both at top of the column) were observed. Obviously, the packed column could not deliver the enhanced mass transfer as expected (from the high contacting area). Due to the path blockage in packed column, bubble was allowed to move more slowly. It resulted in slower slip velocity expressed as a smaller k (mass transfer coefficient) in following equation:

$$Sh = \alpha \, Re^{\beta} \, Sc^{\gamma} \qquad (4.4)$$

where Sh = Sherwood number

Re = Reynolds number

Sc = Schmidt number

Equation (4.4) can be formulated to

$$\frac{kd}{D} = \alpha\left(\frac{\rho v D}{\mu}\right)^{\beta}\left(\frac{\mu}{\rho D}\right)^{\gamma} \qquad (4.5)$$

where k = Mass transfer coefficient ($m \cdot min^{-1}$)

d = Diameter of column (m)

D = Mass diffusivity ($m^2 \cdot min^{-1}$)

ρ = Fluid density ($kg \cdot m^{-3}$)

v = Slip velocity or mean velocity ($m \cdot min^{-1}$)

μ = dynamic viscosity ($kg \cdot (m \cdot min)^{-1}$)

α, β and γ = constant number

Equation 4.5 suggests that slower silp velocity (v) could cause lower mass transfer coefficient resulting in a decrease in mass transfer rate (N). Fortunately, mass transfer area between gas bubble and liquid (A) was enhanced by packing material. The influence of gas holdup and bubble diameter could be realized from the following analyses.

$$A = 4\pi\left(\frac{d_b^{\,2}}{2}\right)N_B \tag{4.6}$$

where d_B = Bubble diameter (m)

N_B = Number of bubbles

ε_g is obtained from Equation 4.3, and can be re-written in terms of V_g as follows:

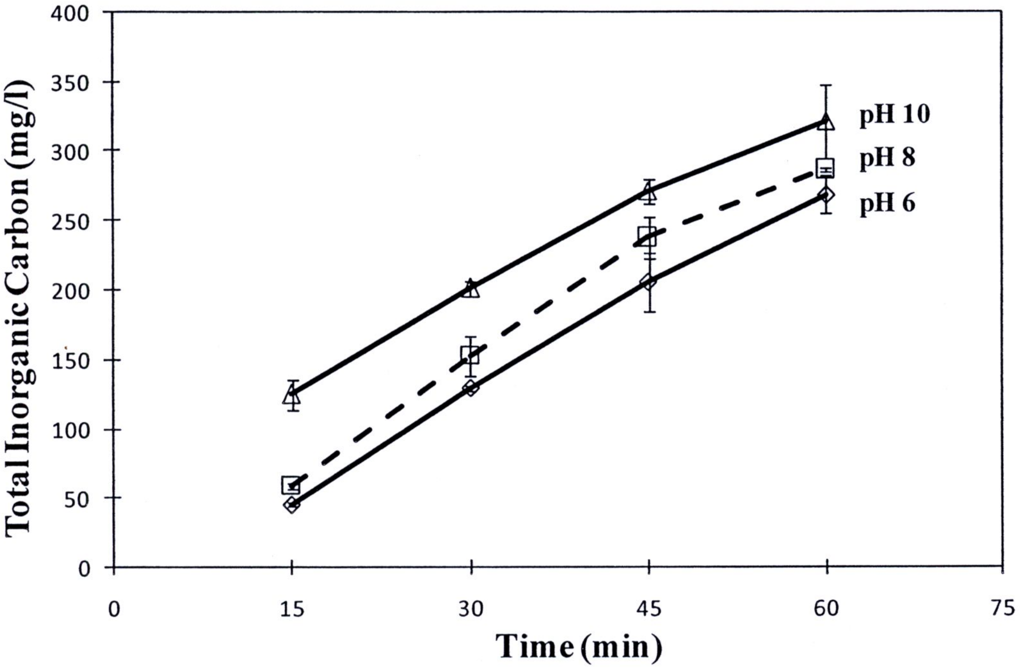
$$\varepsilon_g = \frac{N_B \frac{4}{3}\pi(\frac{d_B}{2})^3}{V_g} \tag{4.7}$$

Substitute N_B from Equation 4.7 to 4.6:

$$A = \frac{3\pi\varepsilon_g V_g}{2d_B} \tag{4.8}$$

From Equation 4.8, an increase in gas hold up (ε_g) would give the better mass transfer rate (N) due to the higher A. However, packing material could cause bubble coalescence resulting in a larger bubble diameter (d_B) which decreased the mass transfer area proportionally. As a result, a twice increase in gas hold up did not enhance the %CO_2 dissolution efficiency as expected. Thus, adding packing material for improving gas-liquid contact area would only result in a slightly better in %CO_2 dissolution efficiency.

(a)



(b)

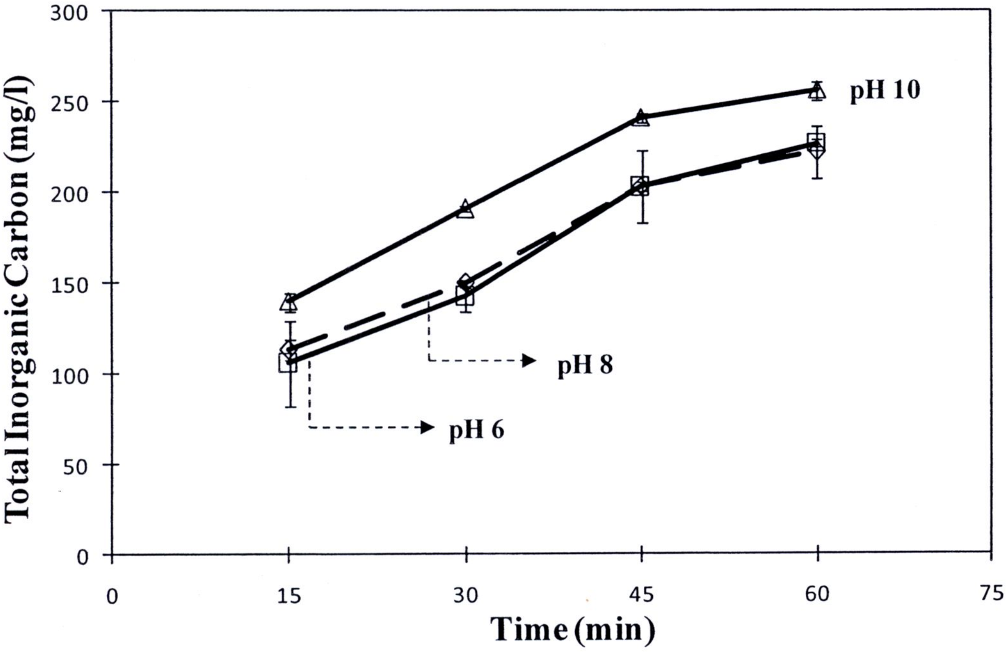


Figure 4.1.2.1 Total Inorganic Carbon time profile at various pH levels in bubble column with packing material **(a)** at top of the column **(b)** at middle of the column

Table 4.1.2 % Efficiency of CO_2 dissolution in packed column at various pH levels and positions

Time (min)	%Efficiency (Carbon Balance)					
	pH 6		pH 8		pH10	
	Top	Mid	Top	Mid	Top	Mid
15	16.83	21.77	42.00	39.33	46.15	51.87
30	23.93	28.22	27.80	26.47	37.21	35.33
45	25.37	29.32	25.11	25.05	33.41	29.83
60	24.84	26.53	20.58	21.04	29.76	23.74

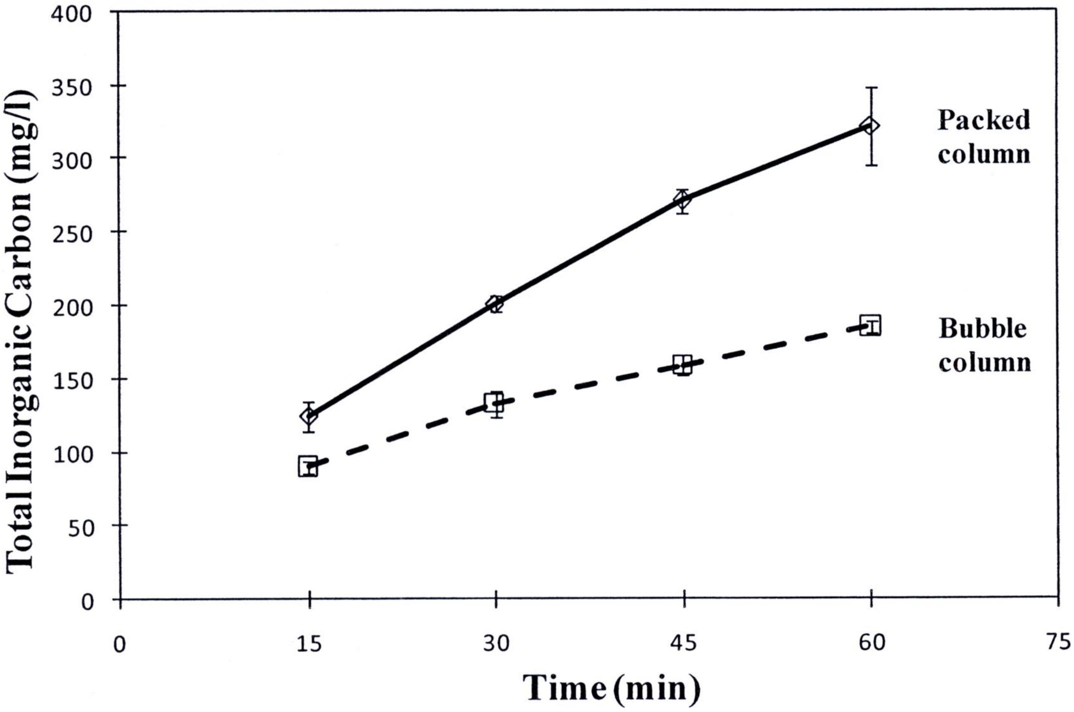


Figure 4.1.2.2 Total Inorganic Carbon time profile at pH 10 level in different column

4.1.3 Effect of gas-liquid contacting area on total inorganic carbon at pH 10 in 3 m high packed column

In this section, the fully packed column height was further upscaled from 1 m to 3 m to study the effect of height on CO_2 dissolution. TIC samples were collected and analysed at every 1m height interval and the associate %Efficiencies were calculated. Note that the experiments were operated at pH 10. The resulting TIC time profile is illustrated in Figure 4.1.3 where TIC increased with time and accumulated in the packed column. Because of inadequate contacting time at the beginning of the experiment, the 15th min TIC at different heights were not significantly different from each other. The 30th min TIC at 1 m height increased substantially and made the highest TIC concentration than at any other positions which could have resulted from the high concentration difference driving force at early stage as discussed earlier. At higher positions and later time period, the dissolved CO_2 (C_l) became high, lowering the concentration difference ($\triangle C$) and so the mass transfer rate. However, CO_2 at 2 and 3m positions after 30 min was able to dissolve more steadily than at 1 m position as C_l only increased gradually with time leading to a larger $\triangle C$ at the beginning, resulting in a steeper slope. Additionally, packed column allowed CO_2 to dissolve more effectively. As a large quantity of CO_2 was dissolved at the lower position, a lesser CO_2 was present at the top position. Therefore a lower TIC was also observed at the top position as a result. It should be noted that an increase in the column height may exhibit some influential factor to the mass transfer as the absolute pressure at 1 m location in the 3 metre column will be about 20% higher than the pressure at 1 m location in the 1 m or 2 m contactors. Increasing the pressure might have considerable effect to the bubble size and mass transfer rate and this was reflected in the higher initial mass transfer of CO_2 from gas to liquid.

%CO_2 dissolution efficiencies at different heights were computed and shown in Table 4.1.3. Clearly, efficiency at 1 m height was better than at 2m and 3m. The highest %efficiency at 1 m height was obtained at 30 min. However, computed %efficiencies at 2 m and 3 m increased with time from 15 min and achieved the highest %efficiency at 45th min. There were not significant differences between %efficiency at 45th and 60th min for both at 2 m (26.95% and 23.47%) and 3 m (19.41% and 17.51%) heights. Furthermore, at 30th, 45th and 60th min, around 23-26% efficiency at 2 m position and around 10-19% efficiency at 3 m position were achieved.

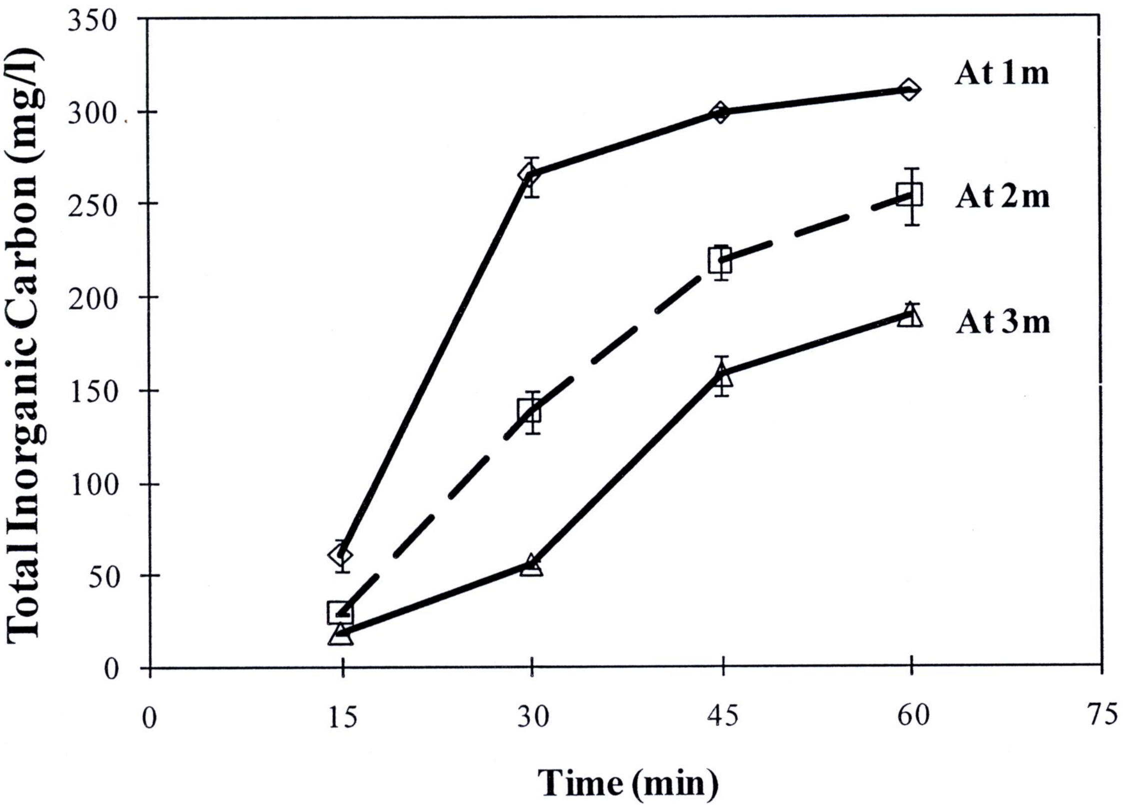


Figure 4.1.3 Total Inorganic Carbon time profile: samples collected various axial positions in the 3 meter high packed column

In summary, %efficiency was the lowest at the beginning and best at 30th min where the highest total % efficiency was obtained here at 78.39%. A triple increase in column height could result in better %efficiency but not triple times, e.g. 29.76% at 1 m high packed column (Table 4.1.2) and 64.35% at 3 m high packed column (at 60th min).

Table 4.1.3 % Efficiency of CO_2 dissolution in packed column at pH 10 and every 1 meter position

Time	%Efficiency (Carbon Balance)			
(min)	1m	2m	3m	Total
15	20.72	9.94	6.27	36.92
30	45.25	23.59	9.54	78.39
45	34.04	24.88	23.29	76.83
60	26.52	21.67	21.02	64.35

4.1.4 Effect of gas flowrate on CO_2 dissolution from 10-40 cc·min^{-1} fed into the 1 and 2m high bubble column

Different CO_2 flowrates in range 10-40 cc·min^{-1} were studied in this experiment to find out how gas flowrate affect CO_2 dissolution in the water. The experiment was conducted in 1 and 2 m high bubble columns at pH 10. For the 1 m high bubble column, the samples were collected at the top part of the column whereas, for the 2 m high bubble column, samples were collected at every 1 m height interval and the TIC time profiles at different gas flowrates were constructed as shown in Fig 4.1.4.1 along with the associated %CO_2 efficiencies in Table 4.1.4.1. Dissolved TIC increased and accumulated with time and the gas flow rate of 40 cc·min^{-1} was shown to give the highest TIC level, whilst 10 cc/min exhibited the lowest trend. Besides, the average highest TIC concentration from 40 cc/min gas flowrate was achieved at 218.34 mg·L^{-1} at 60th min. Increasing gas flowrate resulted in a higher TIC concentration trend over time.

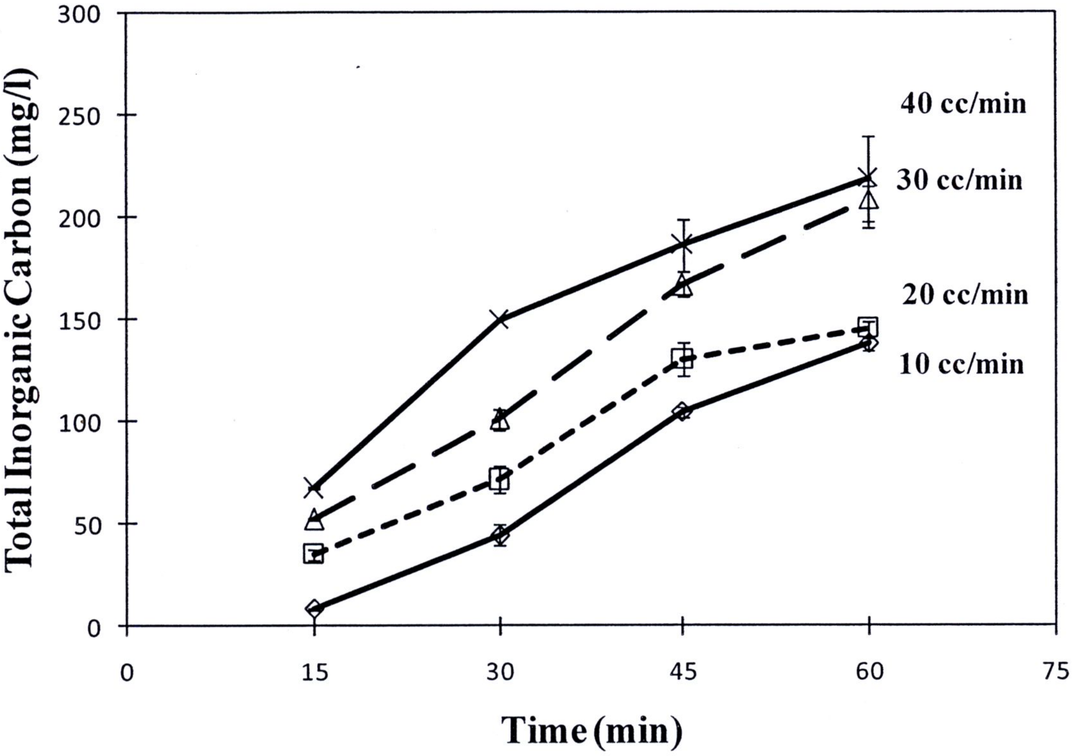


Figure 4.1.4.1 Total Inorganic Carbon at different time in 1 m bubble column: Effect of gas flowrate from 10-40 cc·min^{-1}

However, the calculated %efficiencies in CO_2 dissolution in Table 4.1.4.1 might not suggest an increase of flowrate. %CO_2 efficiency was high in the early stage of experiment and decrease with time for 10 cc·min^{-1}. This effect was not as clear when the flow rate increased to 20-40 cc·min^{-1}, e.g. for 40 cc·min^{-1}, %efficiencies varied in the range of 7.04-8.66. Distinctly, greater gas flowrate exhibited lesser %efficiencies with time and the undissolved gas would be released wastefully. Because of high slip velocity, an increase in gas flowrate was resulted in high mass transfer coefficient and rate. However, this reduced ΔC and made the system equilibrium more rapidly causing a decrease in %efficiency. On the contrary, greater amount of gas per time was could cause the higher C_l appeared in bubble column and higher dissolved TIC concentration.

Table 4.1.4.1 % Efficiency of CO_2 dissolution in 1 m high column

Time	%Efficiency (Carbon Balance)			
(min)	10 cc·min^{-1}	20 cc·min^{-1}	30 cc·min^{-1}	40 cc·min^{-1}
15	30.94	10.64	7.47	8.66
30	29.98	14.71	9.53	7.45
45	23.86	12.27	9.40	7.04
60	21.11	11.02	8.91	7.64

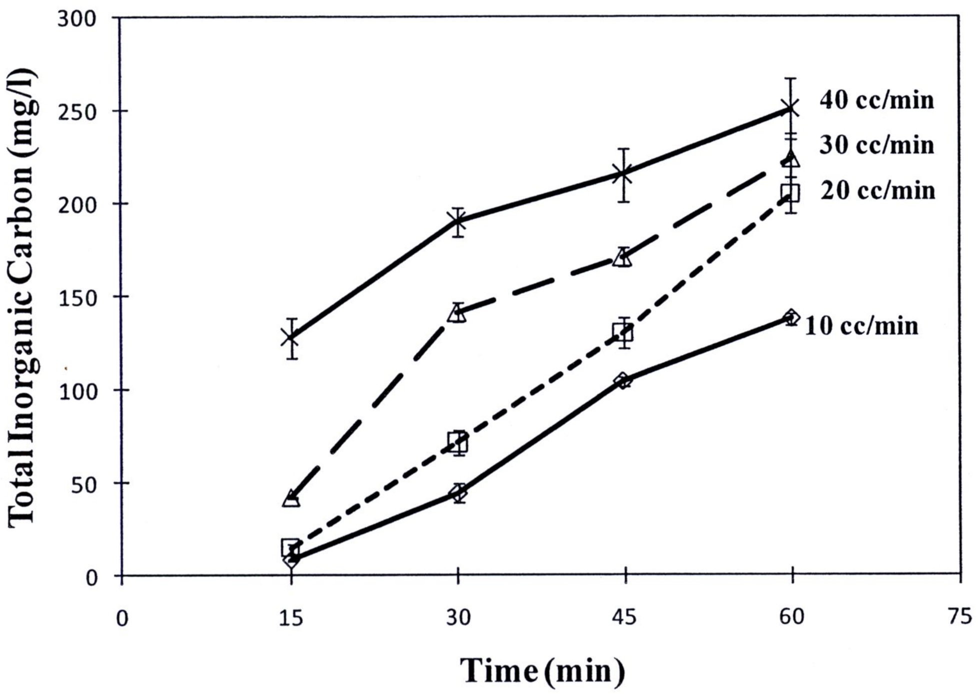
In case of 2 m high bubble column, TIC time profiles at 1 m and 2 m height are shown in Figure 4.1.4.2(a) and 4.1.4.2(b), respectively. Dissolved TIC increased gradually and gathered with the time in the column. At 1 m position, at the beginning of experiment, it was no significant difference in dissolved TIC during the first 45 min as displayed in Figure 4.1.4.1(a). Similar to previous experiment in 1 m high column, an increase in gas flowrate would result in greater TIC dissolved in the water. The average highest TIC concentration was achieved at 60th min at 40 cc·min^{-1} was 264.14 mg·L^{-1}. TIC concentration measured at 1 m high position in the 2 m column was in a similar range with that at the top of the 1 m column regardless of the flowrate employed. Nevertheless, an increase in the gas flowrate could be wastefully released as %efficiency of CO_2 dropped as shown in Table 4.1.4.2(a). In other words, the 10 cc/min gas flowrate provided the most efficient flowrate than any other flowrate where 30.94% efficiency was the highest obtained at 15th min.

Figure 4.1.4.2(b) represents TIC time profile at 2 m or at the top position where samples were collected. TIC trend at the top of the column (2 m) behaved slightly different from that at the middle of the column (1 m) (in Figure 4.1.4.2(a)). To begin with, in the first 30 min, the TIC concentrations at the top and middle parts were close at all flowrates. The deviation started to be well observed after 30 min where the 40 cc/min TIC provided the highest average TIC concentration of 250.10 mg·L^{-1} at 60th min. The increase in TIC at higher gas flowrate could be due to the accelerating bubble velocity which facilitated the gas-liquid mass transfer (as long as the system behaves in the bubbly flow regime). In contrast, the gas flowrate of 10 cc·min^{-1} gave the lowest level of dissolved TIC. Despite so, %Efficiencies of CO_2 dissolution was found to be the highest at 10 cc·min^{-1} as most of CO_2 in the inlet gas stream could dissolve into the water (Figure 4.1.4(b)). On the other hand, a greater quantity of CO_2 did not have enough contact time with the solution and was wastefully released to the atmosphere.

In addition, bubble column always exhibited the plug flow – like behaviour at low gas throughput. This behaviour gradually changed to the well mixed as the gas flowrate increased. As a result, greater gas flowrate led to the accumulation of dissolved TIC at the top of the column due to higher velocity and greater bubble diameter. Figure 4.1.4(a) and 4.1.4(b) depicts that there were large differences between the axial TIC concentrations (i.e. at 1 m and 2 m height) particularly at low gas flowrates (10 and 20 cc·min^{-1}), and the differences seemed to be insignificant at higher gas flowrates (40 cc·min^{-1}). This could be due to the different mixing behaviour as the higher flowrate seemed to be able to induce more back-mixing and the behaviour of the system became closer to the completely mixed pattern. On the other hand, the column behaved closer to a plug flow mode at low gas flowrate.

In sumary, an increase in gas flow rate might enhance the CO_2 solubility, but at this condition, most of the CO_2 was just released to the atmosphere, resulting in the low %efficiency in CO_2 dissolution. Hence, it might not be worthwhile to feed the gas at high flowrate into the bubble column. Besides, an increase in height without adding gas contacting area could not effectively provide a satisfactory level of efficiency in CO_2 dissolution (when compared with the shorter column).

(a)



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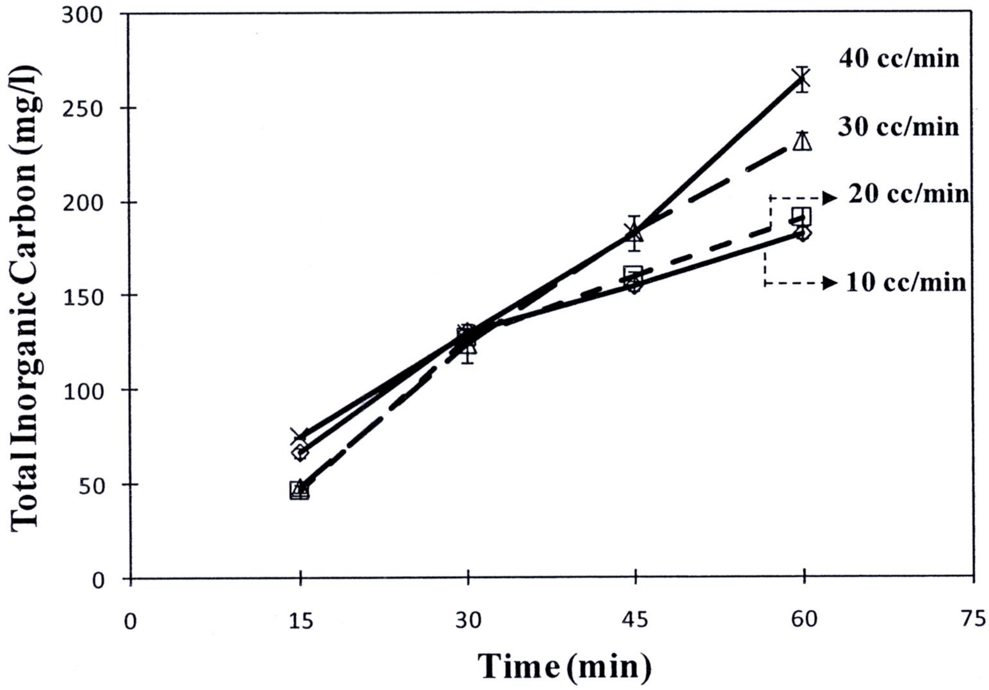

Figure 4.1.4.2 Total Inorganic Carbon at different time: effect of gas flowrate from 10-40 cc·min^{-1} on Total Inorganic Carbon concentration and samples collected (a) at 1m height (b) at 2m height

Table 4.1.4.2 (a) % Efficiency of CO_2 dissolution in 2 m high column: samples collected at 1 m position

Time	**%Efficiency**			
(min)	**10 cc/min**	**20 cc/min**	**30 cc/min**	**40 cc/min**
15	30.94	10.64	7.47	8.66
30	29.98	14.71	9.53	7.45
45	23.86	12.27	9.40	7.04
60	21.11	11.02	8.91	7.64

Table 4.1.4.2 (b) % Efficiency of CO_2 dissolution in 2 m high column: samples collected at 2 m position

Time	**%Efficiency**			
(min)	**10 cc·min^{-1}**	**20 cc·min^{-1}**	**30 cc·min^{-1}**	**40 cc·min^{-1}**
15	4.08	3.44	6.49	14.79
30	10.31	8.27	10.88	11.00
45	16.09	10.05	8.79	8.29
60	15.95	11.81	10.34	7.23

4.1.5 Effect of salinity on CO_2 dissolution

CO_2 dissolution in the salt water has great application as many microalgae are marine species and their growth would require the carbon source in some particular forms. Various salinity levels from 0 to 30 ppt (part per thousand) were carried out in this experiment. The pH value of the fresh control experiment was set at pH 8 which was the closest to that of the brine solution. An experiment was taken place in the 1 m high bubble column. Dissolved TIC was increased with time and was accumulated in the bubble column. The presence of salinity lowered the dissolution of TIC in the solution. Clearly, the highest salinity in this experiment, 30 ppt, resulted in lowest TIC trend than others. For fresh (0 ppt) and brackish water (5 ppt), TIC was not quite distinctly different at the beginning but the difference became clearer at the later stage of the experiment. %efficiency of CO_2 dissolution at various salinity levels is reported in Table 4.1.5. The highest %efficiency at every time sample collected was achieved at zero level of salinity (fresh water) whereas the highest salinity in this experiment, at 30 ppt, exhibited the lowest %efficiency than the others. Higher degree of salinity means water contains higher dissolved salt contents, e.g. sodium chloride, magnesium and calcium sulfate. These might lower the solubility, especially at higher degree of salinity. As the result, CO_2 solubility become lower than that observed in fresh water.

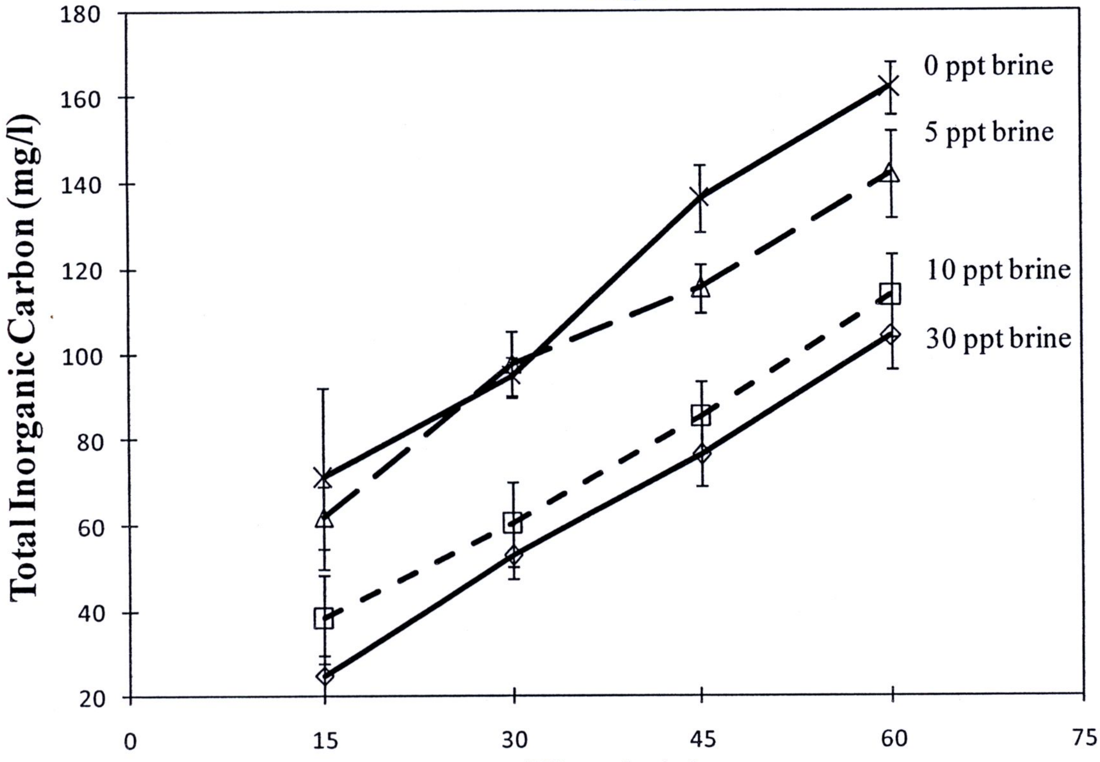

Figure 4.1.5 Total Inorganic Carbon time profile and salinity levels from 0-30 ppt

Table 4.1.5 %Efficiency of CO_2 dissolution at various salinity levels from 0-30 ppt

Time	**%Efficiency**			
(min)	**0 ppt**	**5 ppt**	**10 ppt**	**30ppt**
15	35.83	31.19	19.24	12.51
30	26.31	27.09	15.19	13.32
45	25.20	19.38	14.32	12.82
60	22.47	17.88	14.31	13.13

4.1.6 CO_2 dissolution using Circulating Counterflow Contactor (C.C.C.)

Previously, the effects of pH, liquid-gas contacting area, column height and gas flowrate were studied for their influence on the dissolution of CO_2 in the water. In this section, the optimal combined effects led to the new cooperated system design; it was thereafter called "Circulating Counterflow Contactor- C.C.C" 1 m packed column was implemented and the flow configuration was changed from static to recycle flow in which it allowed gas and water to contact in opposite direction in the reactor. The 5 litres reservoir was united in the flow system to allow a more effective recirculation of the water. The recirculating liquid flowrate was varied from 1 to 3 LPM (Litres per minute), gas flow rate was controlled at 10 cc/min and the pH at 10. Figure 4.1.6 demonstrates the TIC time profile at different recirculating flowrates whereas Table 4.1.6 reports the %efficiency of the system. TIC increased with time and accumulated in the column, and the recirculating flowrate that gave the highest TIC concentration was 2 LPM. The highest %efficiency was achieved at 56.01% at the first 15 minutes but this seemed to slightly decrease with time.

The better CO_2 dissolution with C.C.C. system was resulted from two particular reasons; (1) an increase in slip velocity due to the recycle flowrate of liquid and (2) the diminishing concentration difference ($\triangle C$) barrier. Firstly, applying of recirculating flowrate of liquid from the top of the column in the transverse direction with gas resulted in gas bubble being in contact with liquid at a longer time period, allowing gas to dissolve in liquid more. Additionally, gas bubbles did not show coalescing behaviour in such dynamic condition when compared with that in the static condition. This resulted in a smaller bubble, or higher mass transfer area which consequently provided a higher mass transfer rate. For the second reason, larger $\triangle C$ was found in this system as the more well mixed condition lowered the average C_l leading to a greater concentration different driving force. Thus, high % CO_2 dissolution efficiencies could be found not only the early stage but also at the later stage.

From these reasons above, C.C.C. might be the successful combined effect for CO_2 dissolution system in which the most optimal recycle flowrate was employed at 2 LPM. Next, utilize captured CO_2 for microalgal cultivation purpose will be studied in section 4.2.

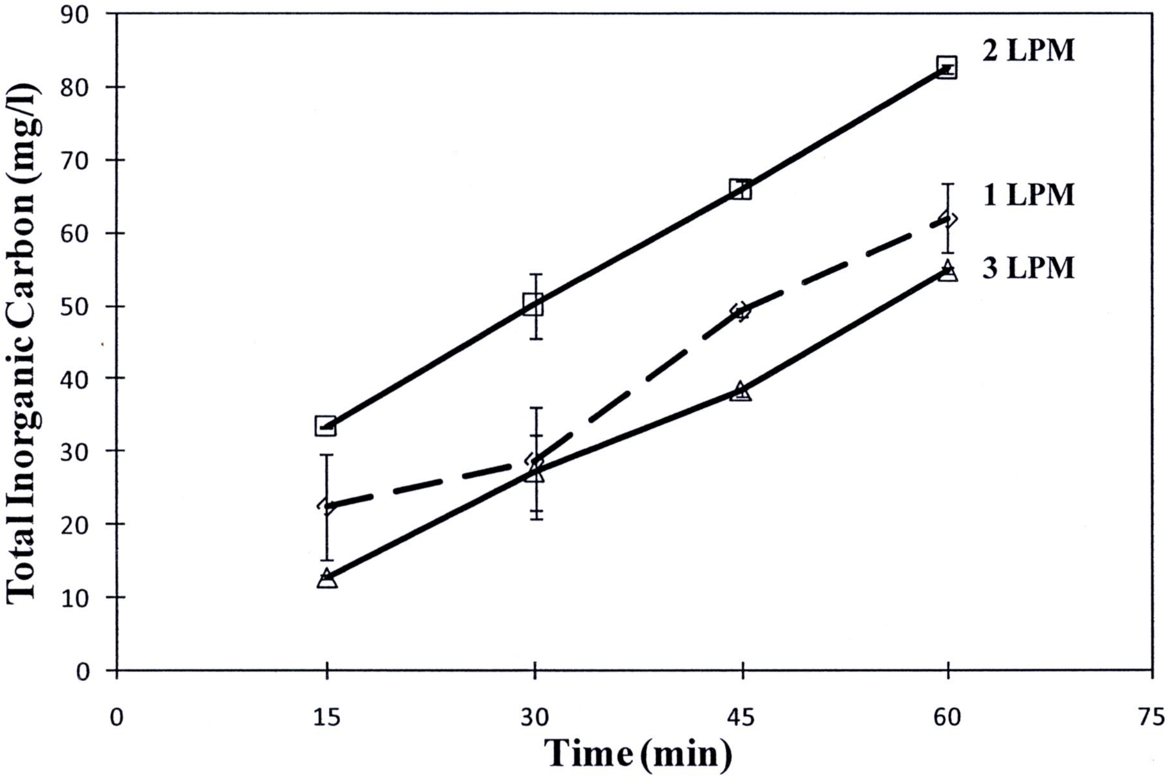

Figure 4.1.6 Total Inorganic Carbon at different time at various recirculating flows in the gas-liquid contacting bubble column, using recycle flow in a range of 1-3 LPM (Litres per minute)

Table 4.1.6 %Efficiency of CO_2 dissolution using recycle flow of 1-3 LPM

Time (min)	%Efficiency		
	1 LPM	2 LPM	3 LPM
15	37.56	56.01	21.40
30	23.92	42.05	22.80
45	27.54	36.90	21.47
60	26.06	34.70	23.02

4.2 Accelerating microalgal growth with bicarbonate as inorganic carbon source

4.2.1 Cultivation of C. vulgaris with $NaHCO_3$ at various pH range

The cultivation of *Chlorella vulgaris* was investigated in various range of pH cultivating condition. Originally, modified M4N (Morita et al., 2000) is reported to be suitable for the growth of *Chlorella vulgaris*, and this medium, without the addition of $NaHCO_3$, was employed as a blank experiment. Note that this medium is without the presence of $NaHCO_3$ and the carbon source is the CO_2 from aeration. Unlike CO_2, bicarbonate ion (HCO_3^-) can be dissolved well in the water due to its high solubility and it is the aim of this work to investigate whether this readily soluble form of carbon (bicarbonate) benefit the growth of such alga. Importantly, using bicarbonate compound for microalgal cultivation requires that the pH of the solution be initially adjusted to a proper range, and it was examined in this section how the pH could affect the growth of the alga. To achieve this, $NaHCO_3$ at 30 ppm was added to the medium at various initial pH (from 6 to 9). Cell concentration time profile illustrated in the Figure 4.2.1 displayed the experimental results. It took approximately 6 days for the cell to reach its stationary phase where the averaged maximum cell concentration achieved from pH 6, 7, 8 and 9 conditions were 106, 105, 73.75 and 42.13 million cells per millilitre, respectively. pH around 6 and 7 seemed to give the best cell growth above which the growth started to drop, and it was obvious that pH 9 was, by all means, not suitable for cell growth (as some of the bicarbonate can be transformed to carbonate which could not be uptaken by the cell). It is interesting that the cultivation at pH 8 gave a better result than the blank test in which the initial pH was around 7.2. The growth rate can be calculated from the log phase period as the specific growth rate (μ) in unit h^{-1} and d^{-1} and shown in Table 4.2.1. The highest specific growth rate was acquired at 0.045 h^{-1} or 1.080 d^{-1} at pH 7. 0.043 h^{-1} or 1.032 d^{-1} at pH 6, 0.040 h^{-1} or 0.960 d^{-1} at pH 8 and 0.034 h^{-1} or 0.816 d^{-1} at pH 9.

Distinctly, enhancing microalgal growth with bicarbonate as inorganic carbon for microalgal cultivation offered the higher maximum cell concentration and specific growth rate compared with the case without bicarbonate (blank test). From the finding, suitable initial pH value for *C. vulgaris* cultivation was in the range of 6-7 in which utilization of bicarbonate was most effective.

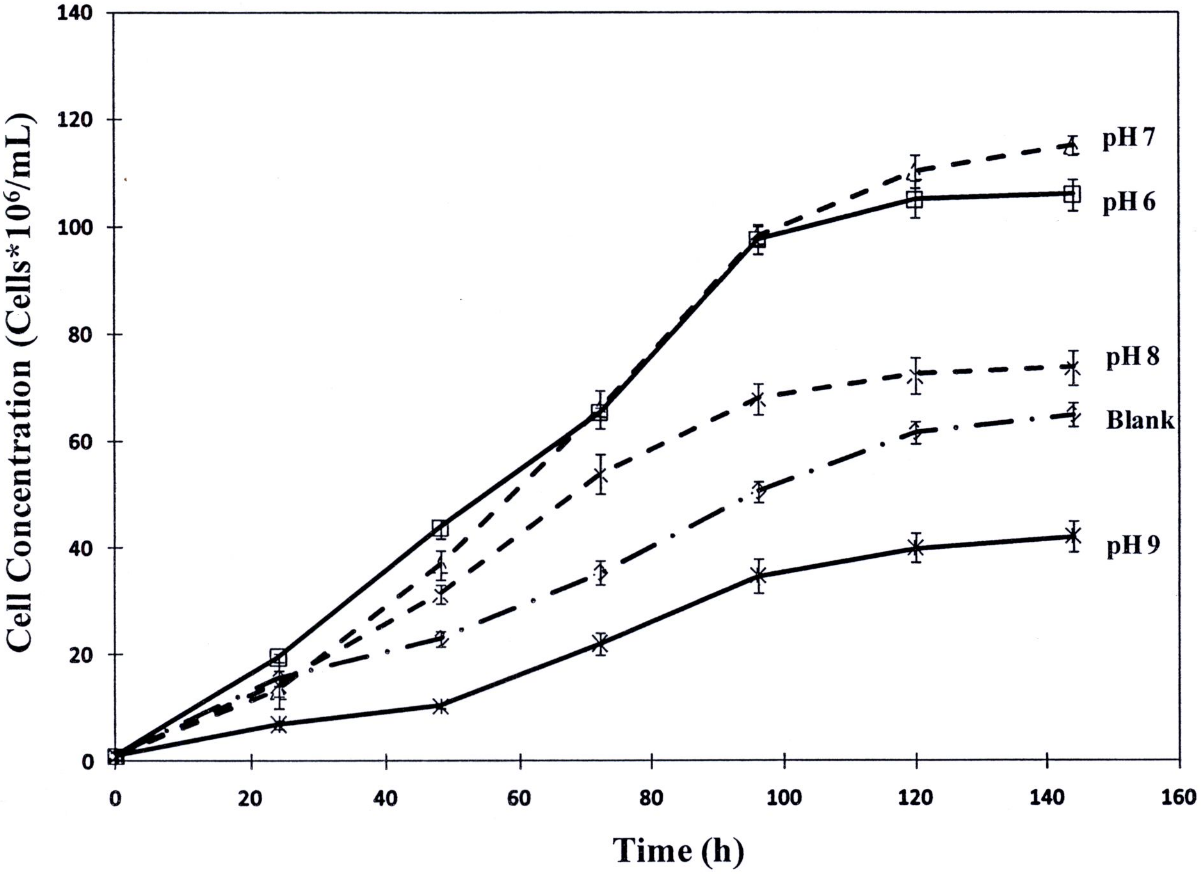

Figure 4.2.1 Growth curve of *Chlorella vulgaris* cultivation with 30 ppm $NaHCO_3$ as inorganic carbon at various pH ranges from 6-9

Table 4.2.1 Maximum cell concentration and specific growth rate (μ) of *Chlrollera vulgaris* cultivation with 30 ppm $NaHCO_3$ as inorganic carbon source at various initial pH conditions

Condition	Maximum cell conc. (cells*10^6 ml^{-1})	μ (h-1)	μ (d-1)
Blank	65	0.036	0.864
pH 6	106	0.043	1.032
pH 7	115	0.045	1.080
pH 8	74	0.040	0.960
pH 9	42	0.034	0.816

4.2.2 Cultivation of *C. vulgaris* with high concentration of $NaHCO_3$ and CO_2 dissolved water form C.C.C. as inorganic carbon at pH 7

In this section, initial adjusted medium at pH 7 was employed with higher concentration of $NaHCO_3$, i.e. from 30 to 200 mg·L^{-1} (ppm) to investigate its effect on microalgal growth. In addition, the pH-adjusted CO_2 dissolution water from the C.C.C. system in Section 4.1.5 (at 2 LPM) was also employed to cultivate the alga. It is noted that this solution contained approximately 80 ppm of TIC. Besides, the cultivation with equivalent concentration of $NaHCO_3$ at 80 ppm was also conducted to compare the result with the medium with CO_2 dissolution water. Cell concentration time profile with different amounts of bicarbonate is shown in Figure 4.2.2.

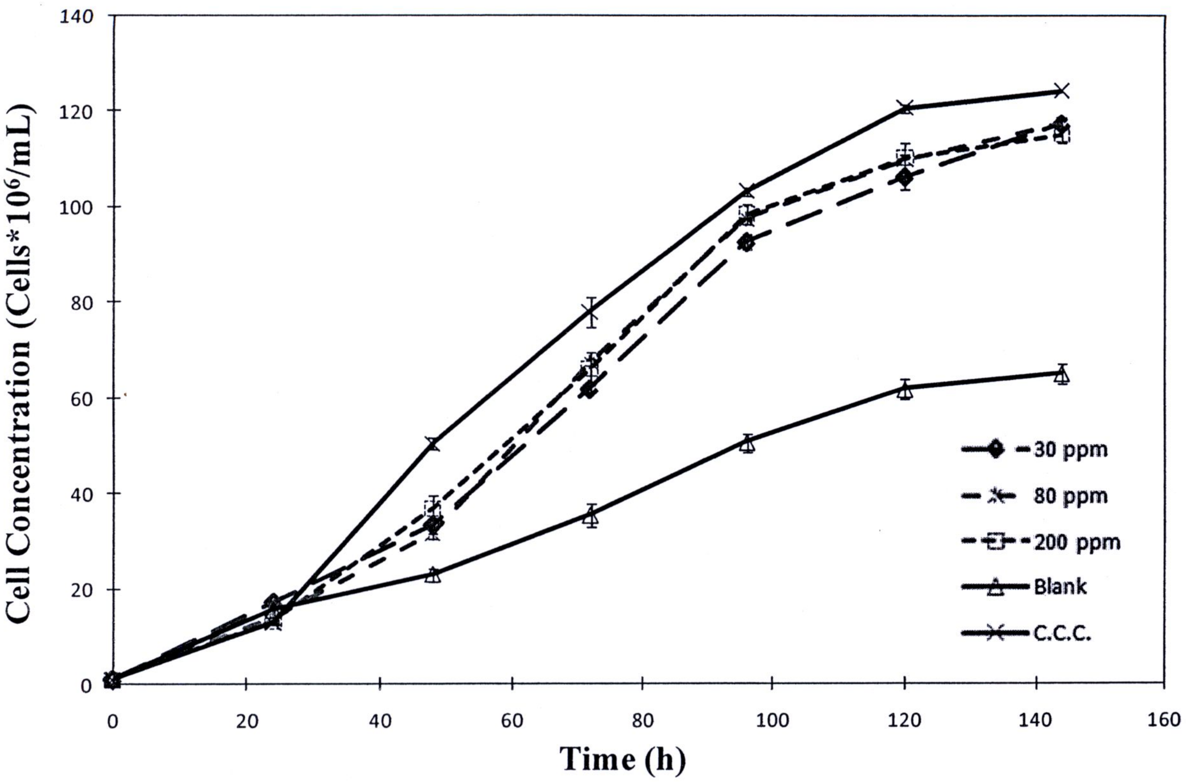

Figure 4.2.2 Growth curve of *C. vulgaris* cultivated with various 0, 30, 80 and 200 ppm $NaHCO_3$ and water from CO_2 dissolved water from C.C.C. as inorganic carbon at initial pH 7 condition

Obviously, the cultivation in blank medium (without $NaHCO_3$) was the lowest which illustrates well that this microalga could uptake the carbon in bicarbonate form. However, not significantly different growth curves were clearly observed from the cultivation with 30, 80 and 200 ppm $NaHCO_3$ where the maximum cell concentrations at the various conditions are reported in Table 4.2.2. Only a slight difference in specific growth rate was obtained; 1.080, 1.056 and 1.032 d^{-1} for the cultivation at 30, 80 and 200 ppm $NaHCO_3$, respectively. However, CO_2 dissolution water from the C.C.C system (at 2 LPM) displayed the greater trend in cell concentration time profile compared with other cultivation with the addition of $NaHCO_3$ where the maximum cell concentration and specific growth rate were obtained at 124 million cells per millilitre and 1.104 d^{-1}, respectively. This verifies that *Chlorella vulgaris* could be well cultivated using carbon source from the solution obtained from the CO_2 absorption column. When compared the results with the medium with 80 ppm $NaHCO_3$, the growth in the C.C.C. water seemed to give a slightly better result, which could be due to the error from experiment.

Table 4.2.2 Maximum cell concentration and specific growth rate (μ) of *Chlrollera vulgaris* cultivation with various amount of $NaHCO_3$ as inorganic carbon source at initial pH 7 condition

Condition	Maximum cell conc. (cells*10^6 ml^{-1})	μ (h^{-1})	μ (d^{-1})
Blank	65	0.036	0.864
30ppm $NaHCO_3$	115	0.045	1.080
80ppm $NaHCO_3$	117	0.044	1.056
200ppm $NaHCO_3$	118	0.043	1.032
C.C.C. water	124	0.046	1.104