

Correlation study of microalgae carbonation in membrane integrated photobioreactor

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Abstract. Microalgae ability to utilise CO₂ higher compared to terrestrial plant making it suitable for biomass production and as CO₂ utiliser. This could be one of many ways to preserve a safer and healthier environment with less air pollutant. For study purposes, CO₂ usually transported to microalgae culture broth with the aid of membrane technology to prevent formation of large bubble and to accelerate the carbonation of microalgal media. However, membrane susceptible to accumulation of CO₂, which can cause extreme acidic to microalgal media. This prevents microalgae to assimilate CO₂. Thus, this study proposes correlations to prevent the extreme acidic: which represents the relationship of: (1) CO₂ inlet and accumulation, (2) CO₂ inlet and CO₂ at the membrane-liquid interphase and (3) CO₂ inlet and CO₂ solubility in the media. The correlations were successfully validated with a deviation of less than 20% compared to the theoretical value.

1. Introduction

The membrane technology has received considerable attention as one of the methods to deliver CO₂ into bioreactor for microalgae cultivation [1,2]. The integration of membrane with bioreactor was reported capable of increasing the microalgal biomass production [3,4]. The biomass are desired to be processed into biofuel, pharmaceuticals product and etc [5].

Another purpose of membrane integration is to increase the CO₂ capture and utilisation by microalgae, which currently under investigation [6]. However, the membrane integration also susceptible to accumulation of CO₂ due to fibre microporous which causes resistance between the gas-membrane, membrane-liquid and gas-liquid interphase in the membrane contactor [7-9]. The accumulation of CO₂ causes extreme acidic to the microalgae culture when pumped out at once off the membrane due to the natural conversion process of CO₂ into carbonate, bicarbonates and acid carbonic [10]. This affects the microalgae growth rate and causes lethal to some microalgae species which have low tolerance of low media pH [11].

The effect of accumulation within the membrane can be avoided by supplying CO₂ at a low concentration but probably will result in insufficient CO₂ for dense microalgae cultured in the bioreactor. Thus, supplying at optimum concentration is the most appropriate way to overcome the problem of accumulated CO₂ in the membrane. However, supplying the optimum CO₂ concentration



requires massive experimental works and yet it depends on the membrane type. One of many ways to predict the accumulation is by correlating the CO₂ inlet (feed) with CO₂ solubility (DCO₂). A correlation to predict the relationship of CO₂ inlet, accumulation and DCO₂ with respect to membrane properties is the most suitable method to overcome the accumulation and CO₂ excess. With the correlation, optimum CO₂ concentration can be supplied accordingly. Thus, this work aims to develop the said correlation.

2. Materials and methods

2.1 Membrane photobioreactor system

The setup of the membrane photobioreactor (PBR) is shown in figure 1.

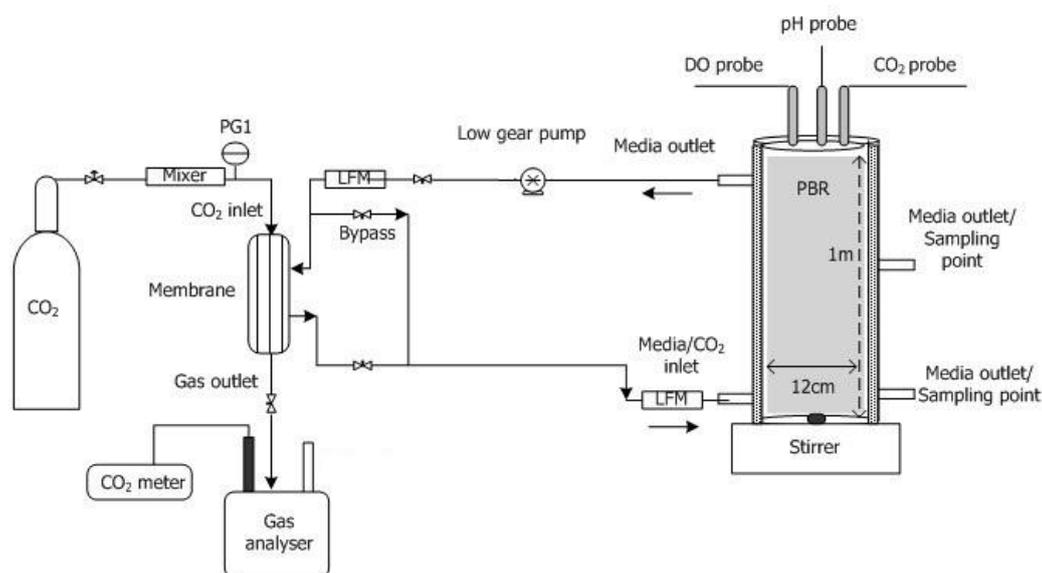


Figure 1. Experimental setup of membrane integrated with photobioreactor, PG: pressure gas, PBR: photobioreactor, LFM: liquid flow rate metre

The membrane that was used to validate the correlation is GFD hydrophobic UFS220 which was made up of 2400 hollow fibre made from polyethylene. The characteristics of the membrane and PBR are listed in table 1.

Table 1. Characteristics of the membrane and PBR.

Features	Membrane	PBR*
Number of fibres	2400	Not applicable
Fibre pore size (μm)	0.5	Not applicable
Length (mm)	495	1000
Total surface area (m^2)	0.80	0.4
Shell internal/PBR diameter (mm)	60	80
Capacity (m^3/s) $\times 10^{-5}$	2.7	Not applicable
Membrane/acrylic thickness (mm)	0.65	3
Shell side/PBR volume (m^3) $\times 10^{-3}$	0.43	23
Volume occupies by hollow fibre (m^3) $\times 10^{-3}$	2.5	Not applicable

The outlet gas of the membrane can be controlled and closed when necessary, according to experimental purpose thus making this membrane physically suitable for the carbonation in microalgal media beside low cost compared to other available commercial membrane in the market. The PBR was operated as a closed system in a controlled temperature at 27°C. The CO₂ and temperature probes and gas analyser were attached in the PBR. The PBR is covered with aluminium foil to avoid any photosynthetic activity that could change the results during the experimental work.

2.2 Microalgal media

This study employs *Chlorella* sp. which was isolated from Tun Fuad Stephens Lake that located at 6°N and 116°E. A modified Jaworski's medium which is lacking in carbon source was used as a medium for the microalgae. The media contained of 0.0124 g/l KH₂PO₄, 0.05 g/l MgS O₄.H₂O, 0.00225 g/l EDTAFeNa, 0.00225 g/l EDTANa₂, 0.00248 g/l H₃BO₃, 0.00139 g/l MnCl₂.4H₂O, 0.001 g/l (NH₄)₆Mo₇O₂₄.4H₂O, 0.00004 g/l Cyanocobalamin, 0.00004 g/l Thiamine HCl, 0.00004 g/l Biotin, 0.08 g/l NaNO₃ and 0.036 g/l Na₂HPO₄.12H₂O. The media and microalgae were mixed in water which was used as liquid phase in the membrane contactor.

2.3 Evaluation of proposed correlation

The correlation was validated by comparison with experimental data. The microalgae density of the media is 0.0401 kg/m³. This value is the most suitable for optimum CO₂ solubility and resulted in low risk of fouling. The CO₂ that accumulates inside the membrane and DCO₂ were measured based on CO₂ mass balance that enter and exit the membrane which directly recorded by the CO₂ probe that attached in the bioreactor. The CO₂ probe is connected to CO₂ metre CGP-31. Note that, the CO₂ metre does not measure the total DIC but total CO₂ that soluble in liquid. Thus, to determine carbonate and carbonic acid, the pH solution was taken simultaneously. The pH is a measure of the total ratio of hydrogen ion (H⁺) to hydroxyl ions (OH⁻) which effective way to measure the carbonic acid and carbonate in the media. The correlation of CO₂ feed and dissolves in the media was measured by subtracting the accumulation of CO₂ inside the membrane. The CO₂ supply is controlled using a CO₂ mixer (see figure 1). On the other hand, CO₂ was supplied in purified grade compressed in 30kg CO₂ cylinder.

3. Theory and calculation

The correlation of CO₂ feed and accumulation with CO₂ that would soluble in a liquid phase in the membrane contactor were developed by first correlating the CO₂ feed with CO₂ concentration that accumulated in the membrane. This follows by correlating CO₂ feed with CO₂ at membrane interphase and maximum solubility in liquid.

3.1 Correlating CO₂ feed with accumulation in the membrane

The inlet and outlet flow rate of CO₂ can be correlated based on mass balance that enter and exit the membrane. The mass flow rate is equivalent with volumetric flow rate multiply with concentration or constant volume multiply with a concentration rate ($\dot{m}_{CO_2} = \dot{V} C_{CO_2}$ or $\dot{m}_{CO_2} = V \dot{C}_{CO_2}$). Thus,

$$\frac{dC_{CO_2(A)}V_m}{dt} = (\dot{V}_{(gi)}C_{CO_2(gi)} + \dot{V}_{(Li)}C_{CO_2(Li)}) - \frac{dC_{CO_2(Lf)}V_{(Lf)}}{dt} - \frac{dC_{CO_2(gf)}V_{(gf)}}{dt} \quad (1)$$

whereas, $C_{CO_2(A)}$, $C_{CO_2(gi)}$, $C_{CO_2(Li)}$, $C_{CO_2(Lf)}$ and $C_{CO_2(gf)}$ are CO₂ concentration that accumulated in the membrane, at gas inlet, at liquid inlet, at liquid outlet and at gas outlet, respectively. The membrane volume on the other hand is represented as V_m . The V_{AG} and V_{AS} are constant volumetric space that can be occupied by gas phase and liquid phase in the membrane, respectively. The symbol of d/dt and \dot{V}_{gi} shows the non-constant and constant variable (volumetric flow rate) variable that changes with time, respectively. Rearranging,

$$V_{AG} \int \frac{dC_{CO_2(AG)}}{dt} + V_{AS} \int \frac{dC_{CO_2(AS)}}{dt} + V_{(Lf)} \int \frac{dC_{CO_2(Lf)}}{dt} + V_{(gf)} \int \frac{dC_{CO_2(gf)}}{dt} = x1 + y1 \quad (2)$$

$(\dot{V}_{gi}C_{CO_2(gi)})$ and $(\dot{V}_{Li}C_{CO_2(Li)})$ are known constant values and symbolized as $x1$ and $y1$, respectively. In this work, the inlet liquid is microalgal media and was assumed has no dissolved CO_2 , thus $\dot{V}_{Li}C_{CO_2(Li)} = y1 = 0$. The feed CO_2 is forced to exit membrane as dissolved CO_2 . Thus, there is no CO_2 outlet in the gas phase ($\frac{dC_{CO_2(gf)}V_{(gf)}}{dt} = 0$) and equation (2) becomes equation (3).

$$\frac{dC_{CO_2(A)}V_m}{dt} = (x1) - \frac{dC_{CO_2(Lf)}V_{Lf}}{dt} \quad (3)$$

The V_{Lf} on the other hand depends on the inlet volumetric flow rate. Since the inlet volumetric flow rate, V_{Li} was constant, the V_{Lf} can be considered as constant as well. Note that, \dot{V}_{Li} is the volume flow rate of inlet liquid obtained from $(\dot{V}_{Li} \times \text{time taken} \times a)$. The \dot{V}_{gi} is the volume flow rate of inlet gas respectively. The outlet liquid V_{Lf} lowers compared to V_{Li} about a times due to pressure drop in the liquid side. The a is a constant value found from the comparison of inlet and outlet liquid flow rate in the membrane. The V_{Lf} depends on V_{gi} and membrane conditions. The membrane volumetric space is constant. Thus, integration of equation (3) becomes equation (4).

$$V_m \int dC_{CO_2(A)} + V_{Lf} \int dC_{CO_2(Lf)} = x1 \int dt \quad (4)$$

The $\int_{c_0}^c dC_{CO_2(A)} = V_m C_{CO_2(A)} - 0$ and $\int_0^t dt = t$. Thus, $V_m(C_{CO_2(A)}) + V_{Lf}(C_{CO_2(Lf)}) = (\dot{V}_{gi}C_{CO_2(gi)})t$. The Henry law stated that the CO_2 that dissolves in liquid can be measured based on: $C_{CO_2(gi)}H = C_{CO_2(Lf)}$. Thus, the equation (1) becomes as in equation (5).

$$C_{CO_2(A)} = \frac{(C_{CO_2(gi)})\sqrt{(\dot{V}_{gi}t - V_{Lf}H)^2}}{V_m} \quad (5)$$

The CO_2 feed into membrane photobioreactor follows the ideal gas theory. Thus, the accumulation also can be predicted based on gas molecular weight (M), flow rate and pressure as follows:

$$C_{CO_2(A)} = \frac{PM_{CO_2}}{RT} \frac{\sqrt{(\dot{V}_{gi}t - V_{Lf}H)^2}}{V_m} \approx \rho_{CO_2} \frac{\sqrt{(\dot{V}_{gi}t - V_{Lf}H)^2}}{V_m} \quad (6)$$

Thus, the equation (5) and equation (6) can be used to predict the accumulation of CO_2 in the membrane.

3.2 Correlating CO₂ concentration at the membrane-liquid interphase

The CO₂ at the membrane–liquid interphase can be defined in term of CO₂ transfer. Figure 2 illustrates the gas flux through the pore of single hollow fibre. The CO₂ flux ($J_{\text{CO}_2(\text{m})}$) through the membrane pore is theoretically affected by varying concentration and working pressure as illustrated in figure 2 (a) [12,13]. The increase in pressure drop is one of the main reasons for the flow rate declines [14]. Figure 2 (a) shows the illustration of flows within the membrane. The higher the pressure in gas side, the slower the flow in liquid side of the membrane. This phenomenon can be explained in term of resistance in the gas side of the membrane. In addition, the driving force of the outlet liquid depends on the pressure gradient between the gas and liquid side [15]. The transport phenomena as introduced by Fick which known as Fick's law can be presented as: $J_{\text{CO}_2(\text{m})} = -D(dC/dx)$ and ideal gas theory [16,17]. The symbol of D represents as a diffusion coefficient, dC is change in CO₂ concentration and dx represents the distance of the CO₂ travels within the membrane. This equivalent to the mass flow rate of gas in kg/s unit that diffused through the membrane pores ($d\dot{m}_{\text{CO}_2(\text{m})}$) divide with membrane-pore surface area (A_{pore}) in m² unit and can be presented as follows:

$$J_{\text{CO}_2(\text{m})} = -D \left(\frac{dC}{dx} \right) = - \left(\frac{d\dot{m}}{A_{\text{pore}}} \right) \quad (7)$$

whereas $d\dot{m} = \dot{m}_{\text{CO}_2(\text{i})} - \dot{m}_{\text{CO}_2(\text{m})}$. The $\dot{m}_{\text{CO}_2(\text{i})}$ and $\dot{m}_{\text{CO}_2(\text{m})}$ is the initial mass flow rate of CO₂ in the gas side and CO₂ that diffused or transported throughout the membrane pore that in contact with the liquid side, respectively (see isometric view in figure 2 (b)).

The diffusion flux of gas through hollow fibre membrane has a travel path, dx equivalent to hollow fibre membrane thickness, δ_{m} (illustrated in figure 2). The rationale of this assumption is CO₂ diffuses out of the hollow fibre through the pore wall which made up the membrane. The concentration gradient of CO₂ on the other hand can be measured as $dC_{\text{CO}_2} = C_{\text{CO}_2(\text{i})} - C_{\text{CO}_2(\text{m})}$, $C_{\text{CO}_2(\text{i})}$ is CO₂ initial concentration in kg/m³ that equivalent to the CO₂ supply from external sources such as $C_{\text{CO}_2(\text{gi})}$. The $C_{\text{CO}_2(\text{m})}$ on the other hand is the amount of CO₂ that in contact with the liquid boundary but not dissolve. The mass flow rate can be presented as follows: $\dot{m}_{\text{CO}_2(\text{i})} - \dot{m}_{\text{CO}_2(\text{m})} = D ((C_{\text{CO}_2(\text{i})} - C_{\text{CO}_2(\text{m})})/\delta_{\text{m}}) A_{\text{pore}}$. Finally, the CO₂ concentration at interphase that diffused through the membrane can be measured as follows.

$$C_{\text{CO}_2(\text{m})} = C_{\text{CO}_2(\text{i})} \left(\frac{DA_{\text{pore}} - \dot{V}_{\text{i}} \delta_{\text{m}}}{DA_{\text{pore}} - \dot{V}_{\text{m}} \delta_{\text{m}}} \right) \quad (8)$$

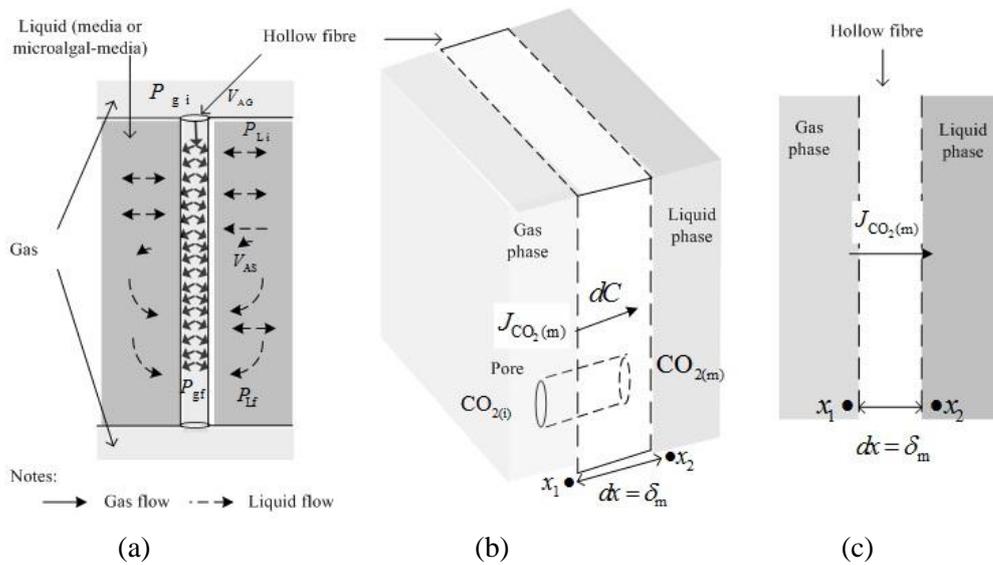


Figure 2. (a) Illustration of gas flow in a single hollow fibre inside the membrane. (b) Illustration of diffusion flux through a hollow fibre pore and (c) Front view of illustration as shown in (b). V_{Ag} : Volume of gas phase in membrane (m^3), V_{AS} : Volume of liquid phase in membrane (m^3), P_{gi} : Inlet gas pressure (bar), P_{gf} : Inlet gas pressure (bar), P_{Li} : Inlet pressure of liquid side (bar), P_{Lf} : Outlet pressure of liquid side (bar). $dx = \delta_m$: membrane thickness, dC : CO_2 concentration gradient, $J_{CO_2(m)}$: CO_2 diffusion flux through the membrane pore, x_1 : first point, x_2 : second point.

The critical part of this correlation is the diffusion coefficient, D which depends on pore wall, porosity and tortuosity. Thus, the equation proposed by Mason and Malinauskas [18] that relates diffusion coefficient of gas in general condition with diffusion coefficient of gas through a membrane pore, $D = D_e (\varepsilon/\tau)$ should be used. For the selected membrane, the hollow fibre average pore diameter is $0.05 \mu m$. The closed up images of the hollow fibre membrane within the membrane module are shown in figure 3.

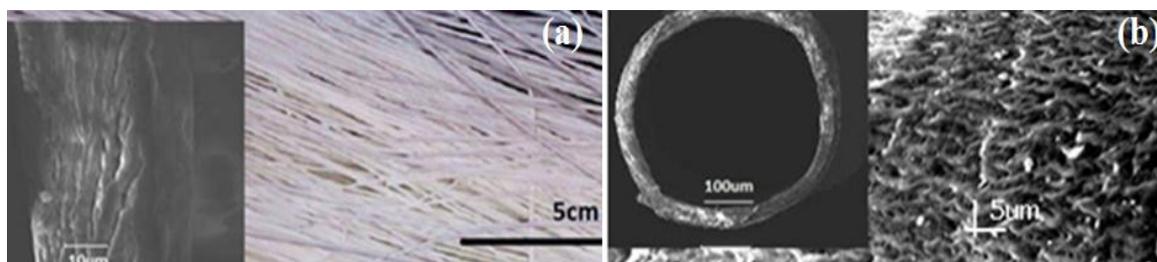


Figure 3. A closed up image of the hollow fibre membrane. (a): Hollow fibres and SEM image of the hollow fibre, (b): SEM image of single hollow fibre and top view of middle-cut hollow fibre

The pore of the tubular shaped-hollow fibre is varied in sphere-like pore (figure 3 (b)). The smaller image in figure 3 (a) is an SEM image of single hollow fibre and in figure 3 (b) is a top view of single hollow fibre. When the pore size of the membrane is smaller compared to mean free path (λ) and the Knudsen number ($K_n = \lambda/d_{pore}$) is larger than one, the CO_2 collides with the pore wall during the diffusion process [19,20]. The λ is measured using correlation proposed by Cunningham and Williams

[21]. The mean free path λ is 0.06 μm and average K_n is 1.35. Thus, the diffusion coefficient follows the Knudsen theory [22]. The diffusion through the membrane pore is more appropriate in term of effective diffusion coefficient as its diffusion affected by pore size, porosity and tortuosity [23]. Thus, the effective diffusion coefficient in membrane is rearranged and expressed as in equation (9).

$$D_e = \frac{D_{\text{MCO}_2} D_{\text{kCO}_2}}{D_{\text{MCO}_2} + D_{\text{kCO}_2}} \quad (9)$$

whereas, D_{kCO_2} represents the Knudsen diffusion and D_{MCO_2} represents the molecular diffusion of CO_2 , which in this case was technically described mathematically using Fick's law. The Knudsen diffusion coefficient is related to kinetic theory of gas and expressed as $D_k = u(d_{\text{pore}}/3)$ whereas u is molecule velocity. The molecule velocity can be related to an ideal gas theory and expresses as $D_k = (d_{\text{pore}}/3)\sqrt{(8RT/\pi M)}$. There are many proposed correlations for Knudsen diffusion coefficient. However, in this work, the correlation that proposed by Cunningham and Williams (1980): $D_{\text{kCO}_2} = 4850d_{\text{pore}}\left(\sqrt{T/M_{\text{CO}_2}}\right)$ was used. The Knudsen diffusion coefficient for CO_2 is $6.33 \times 10^{-2} \text{ cm}^2/\text{s}$.

3.3 Overall mass transfer coefficient of CO_2

The CO_2 is in a gas phase within the membrane pore. Thus, the standard molecular diffusion coefficient or simply the diffusion coefficient of CO_2 in the air is $1.39 \times 10^{-1} \text{ cm}^2/\text{s}$. The overall effective diffusion coefficient is $4.35 \times 10^{-2} \text{ cm}^2/\text{s}$, porosity is 0.8 and tortuosity is 1.8. The porosity and tortuosity were calculated based on the characteristic of the membrane shown in table 1. The values were used for further calculation of CO_2 at interphase that diffused through the membrane pore, $C_{\text{CO}_2(\text{m})}$. The mass transfer resistance within the membrane pore is almost negligible if no media was introduced into the membrane. This resulted in $\dot{V}_{(\text{CO}_2)\text{i}} \approx \dot{V}_{(\text{CO}_2)\text{m}}$ and can be proved using equation (8) whereas, the inlet CO_2 supply has a similar concentration with CO_2 at intervals between membrane and liquid.

3.4 Prediction of maximum CO_2 that would dissolve in the media

The CO_2 enters at the top of hollow fibre and forced to exit through the pore of membrane wall which in contact with the liquid phase. Note that, the amount of CO_2 that has transferred into liquid phase is equal or lower compared to gas diffused through the membrane pore $\left(\frac{dC_{\text{CO}_2(\text{Lf})}}{dt} \leq \frac{dC_{\text{CO}_2(\text{m})}}{dt}\right)$. Thus, the

CO_2 that would dissolve in liquid phase can be predicted from the amount of CO_2 that diffuses throughout the membrane. In overall, the CO_2 that could dissolve in a liquid is higher compared to solubility without the aid of membrane [1]. The dissolved gas in liquid can be defined in term of diffused CO_2 through the membrane and can be reformulated according to Henry's law: $C_{\text{CO}_2(\text{Lf})} = HC_{\text{CO}_2(\text{m})}$ whereas $C_{\text{CO}_2(\text{m})}$ is concentration of CO_2 diffuses through the membrane pores. The CO_2 that dissolves into media phase can be simply rewritten as in equation (10) or equation (11) regardless of liquid flow rate.

$$C_{\text{CO}_2(\text{Lf})} = HC_{\text{CO}_2(\text{i})} \left(\frac{DA_{\text{pore}} - \dot{V}_{(\text{CO}_2)\text{i}} \delta_{\text{m}}}{DA_{\text{pore}} - \dot{V}_{(\text{CO}_2)\text{m}} \delta_{\text{m}}} \right) \approx \text{Maximum } C_{\text{CO}_2(\text{m})} \quad (10)$$

$$C_{\text{CO}_2(\text{Lf})} = H \left(\frac{m_{\text{CO}_2(\text{m})}}{t} \left(\frac{\delta_{\text{m}}}{D_{\text{m}} A_{\text{pore}}} \right) + C_{\text{CO}_2(\text{i})} \right) \approx \text{Maximum } C_{\text{CO}_2(\text{m})} \quad (11)$$

The DCO_2 in media is a major factor of CO_2 uptake by microalgae as CO_2 can only be consumed in the media by microalgae. Thus, the prediction of CO_2 that would dissolve in the media is important for CO_2 uptake by microalgae.

4. Results and discussion

4.1 Correlation of CO_2 inlet and accumulation in membrane

The governed correlation (equation (5)) was evaluated by comparison with experimental work. Thus, the effects of operating period and gas flow rate of CO_2 accumulation within the hydrophobic membrane were selected for the comparison. Figure 4 (a) shows the comparison of theory and experimental work on CO_2 accumulates with respect to operating period. The CO_2 inlet (\dot{V}_{gi}) is $3.3 \times 10^{-6} \text{ m}^3/\text{s}$, liquid inlet (\dot{V}_{Li}) is $3.3 \times 10^{-5} \text{ m}^3/\text{s}$, CO_2 concentration ($C_{\text{CO}_2(\text{gi})}$) is $1.8 \text{ kg}/\text{m}^3$ and the membrane capacity (V_{m}) is 0.00105 m^3 . The experimental work was conducted in multiple times to constant value and three sets of the experiments are represented as points in figure 4 (a). The theoretical correlation on the other hand is represents the line.

The standard deviation between the experimental data was varied from $0.002 \text{ kg}/\text{m}^3$ to $0.025 \text{ kg}/\text{m}^3$. This resulted in %SD from 5% to 17%. The percentage error between the experiments and theory was less than 16%. The confidence interval (CI) was in the range of -0.018 and +0.196 which, was calculated with 80% of confidence level. This value indicates that there is 80% certainty that the real value of the accumulated CO_2 is not more than $0.196 \text{ kg}/\text{m}^3$ and not less than $0.018 \text{ kg}/\text{m}^3$ for an operating period of 5s to 55s. For instance, when the carbonation process took about 5s of the operating period, at $\dot{V}_{\text{gi}} : 3.3 \times 10^{-6} \text{ m}^3/\text{s}$, $\dot{V}_{\text{Li}} : 3.3 \times 10^{-5} \text{ m}^3/\text{s}$, CO_2 inlet concentration: $1.8 \text{ kg}/\text{m}^3$ and membrane capacity is 0.00105 m^3 , the accumulation will not less than $0.047 \text{ kg}/\text{m}^3$ and not more than $0.052 \text{ kg}/\text{m}^3$.

The percentage error which defined as the difference between the theory and experiment value in this work is in the range of $\pm 10\%$ to $\pm 16\%$. The governed correlation is less than 20%. It is agreeable that less than 20% of theory and experiment different is acceptable to validate the correlation [24]. Since, this correlation was governed to predict the accumulation of CO_2 in the membrane so that, right CO_2 feed can be supplied accordingly without causing lethal to microalgae in a bioreactor. Thus, the 20% difference of the real accumulated value within the membrane can be considered as safe to the microalgae. The experimental data shows that suitable working period will result in less than 50% accumulation rate.

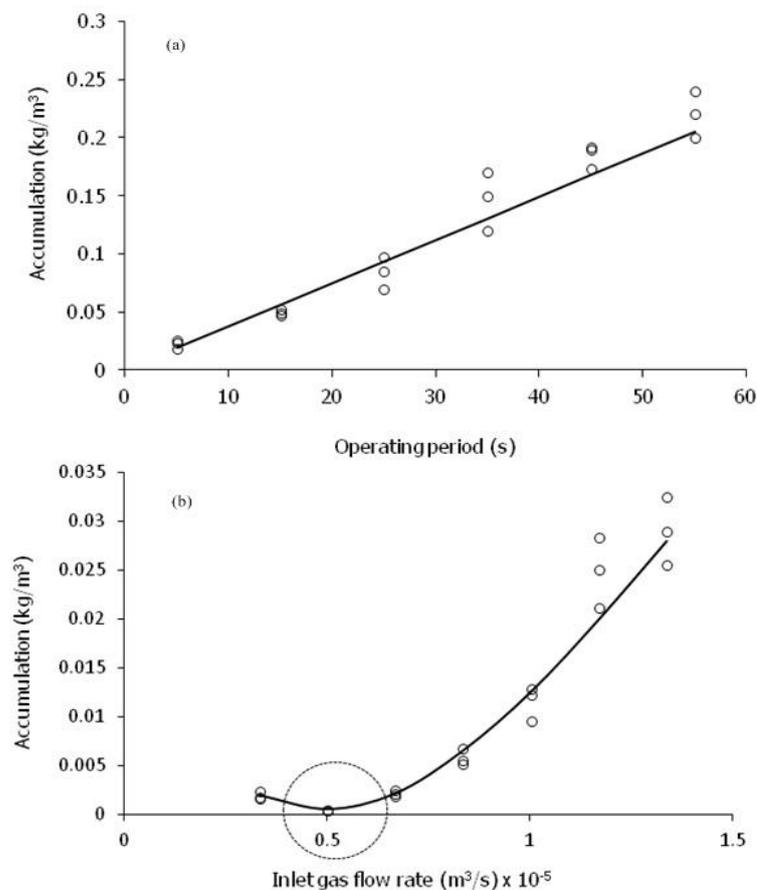


Figure 4. (a) Accumulation of CO₂ with respect to operating period; (b) accumulation of CO₂ with respect to gas flow rate.

The governed correlation also supported by the comparison on the accumulation as a function of gas flow rate when operated at constant liquid inlet and membrane volumetric capacity. The experiment was conducted at $V_m = 1.05 \times 10^{-3} \text{ m}^3$, \dot{V}_{gi} is in the range of $3.34 \times 10^{-5} \text{ m}^3/\text{s}$ to $1.3 \times 10^{-5} \text{ m}^3/\text{s}$ and \dot{V}_{Li} : $3.3 \times 10^{-5} \text{ m}^3/\text{s}$, with an operating period equivalent to 48s. The result was compared and shown in figure 4 (b). The experimental work was conducted in multiple times to achieve a constant value and three sets of the experiments represented as points in figure 4 (b). The line on the other hand is represented as the theoretical value. The %SD between the data is varied from 12% to 19%. The percentage difference of the experimental data was in the range of 2% to 19% compared to theoretical values. Notice that, the lowest accumulation is at $0.5 \times 10^{-5} \text{ m}^3/\text{s}$ as circled in figure 4 (b). This indicates that at \dot{V}_{Li} : $3.3 \times 10^{-5} \text{ m}^3/\text{s}$, the most suitable CO₂ gas flow rate is $0.5 \times 10^{-5} \text{ m}^3/\text{s}$.

4.2 Limitation of the correlation of CO₂ inlet and accumulation

The governed correlation was validated based on the operating period and the gas flow rate. This parameter was selected as it has a major impact on the accumulation of CO₂ in the membrane. However, this correlation was governed without taking consideration on fouling that might occur in the membrane due to microalgae cell, in which the fouling reduce the flow rate at the liquid side.

The governed correlation has considered a function of $V_{Lf} = aV_{Li}$ with a as 0.2. This function is limited to $V_{Lf} = aV_{Li}$ that was analysed for \dot{V}_{Li} lower than $5 \times 10^{-5} \text{ m}^3/\text{s}$ and \dot{V}_{gi} is lower than $1.67 \times 10^{-5} \text{ m}^3/\text{s}$ as shown in figure 5 (a). Notice that, $a = 0.2$ or $a = 20\%$ is an average of reduction of flow rate as indicates from 15% to 23% in figure 5 (a). Thus, ones have to measure the function of liquid inlet and outlet before using the correlation with regards to microalgae concentration in the media. This

correlation can be improved by adding a function of fouling and microalgae density. However, this work requires lots of work and interesting be explored in the future.

The accumulation of CO₂ within the membrane also can be considered as loss for large scale cultivation of microalgae. As discussed in a previous study, 25% of biomass production cost of microalgae is resulted during the carbonation process [25]. In reality, the process to extract pure CO₂ from industry for cultivation of microalgae is costly [26]. Thus, the lower the accumulation rate, the higher the mass transfer of CO₂ into liquid phase. Thus, the requirement of CO₂ to produce an equivalent - amount of biomass is lower. Other factors that affect the solubility of CO₂ include porosity and membrane pores were not included because this variable has more effect on the solubility instead of accumulation.

4.3 Validation of correlation of maximum CO₂ that would dissolve in the media

The correlation in equation (10) and equation (11) were validated as shown in figure 5 (b). The experiment was conducted with CO₂ inlet (\dot{V}_{g_i}): 3.3×10^{-6} m³/s, liquid inlet (\dot{V}_{L_i}): 3.3×10^{-5} m³/s, CO₂ concentration ($C_{CO_2(g_i)}$): 1.8 kg/m³ and membrane capacity is equivalent to 0.00105m³. The theoretical value in figure 5 (b) is indicated as a linear line and the experimental data are indicated as points. With 80% of confidence level, the probability of the true experimental value lies within 0.017 kg/m³ to 0.057 kg/m³. For instance, at 0.0203 kg/m³ of CO₂ inlet, the true value of CO₂ that would dissolve into the liquid phase is not less than 0.017 kg/m³ and not more than 0.019 kg/m³. The percentage standard deviation between the final three sets data is 2% to 11%. The different of theory and experiment which is defined as percentage error is 4% to 20%. This value shows that the experimental result and theoretical are within the acceptable range for validation of the governed correlation. Thus, the proposed correlation in equation (10) and equation (11) are acceptable to predict the relationship of CO₂ that would dissolve in the liquid phase when using a hollow fibre membrane contactor. The volumetric flow rate of inlet gas and volumetric flow rate of CO₂ in membrane pore affects the CO₂ solubility. The result can be explained in term of resistance at interphase between the membrane and liquid phase. Based on comparison between inlet gas and inlet media, the inlet media flow rate affected by the volumetric flow rate of gas inlet and vice versa. This creates instability in DCO₂ thus causes the experimental value shown a slight exponential trend at high CO₂ gas inlet.

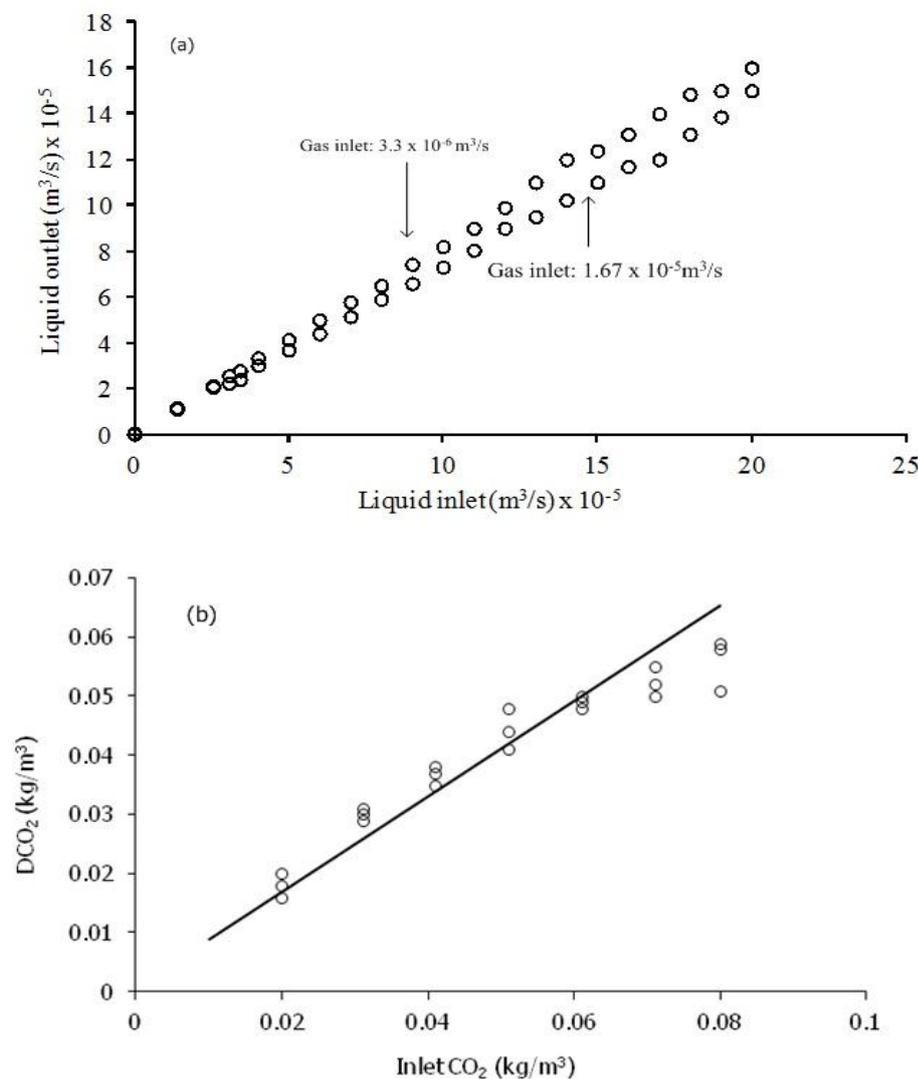


Figure 5. (a) Comparison of liquid inlet and outlet flow rate, (b) Comparison value of DCO₂ between experiment and theory.

4.4 Limitation of the governed correlation

The correlation was validated solely based on Henry constant of CO₂ gas, CO₂ inlet concentration and membrane properties such as thickness and tortuosity. This correlation is used to predict the CO₂ that will pass through the membrane wall from the gas side of the boundary that in contact with liquid side in membrane contactor. The rationale for the governed correlation is the CO₂ concentration that would dissolve into media ($C_{CO_2(Lf)}$) must be equal or smaller compared to CO₂ amount that disused through the membrane ($C_{CO_2(m)}$). However, during the validation work, the amount of CO₂ that would dissolve was assumed in its maximum value ($C_{CO_2(Lf)} = C_{CO_2(m)}$) without taking consideration on the resistance on liquid phase. The liquid phase of the membrane is microalgal media with microalgae concentration approximately 0.0401 kg/m³. Thus, the correlation in equation (10) and equation (11) still can be improved with the addition of function of liquid resistance at different microalgae density. However, the proposed correlation is useful to note the maximum CO₂ that would dissolve in the media regarding on CO₂ inlet concentration. The study on the function of liquid resistance is interesting for future work.

The correlation that was proposed and validated can be summarised and presented as in figure 6. Notice that, the correlations takes consideration mainly on the hollow fibre thickness. The reason for this consideration is most of the membrane resistance in transferring gas to liquid phase is from the interaction of the gas molecule with the membrane wall [27]. The media properties also has become one of the major considerations during the governing process of the correlation which in this study, the properties of microalgal media. This includes the concentration of microalgae in the liquid phase and the flow rate of the liquid phase that passing through the membrane to the bioreactor.

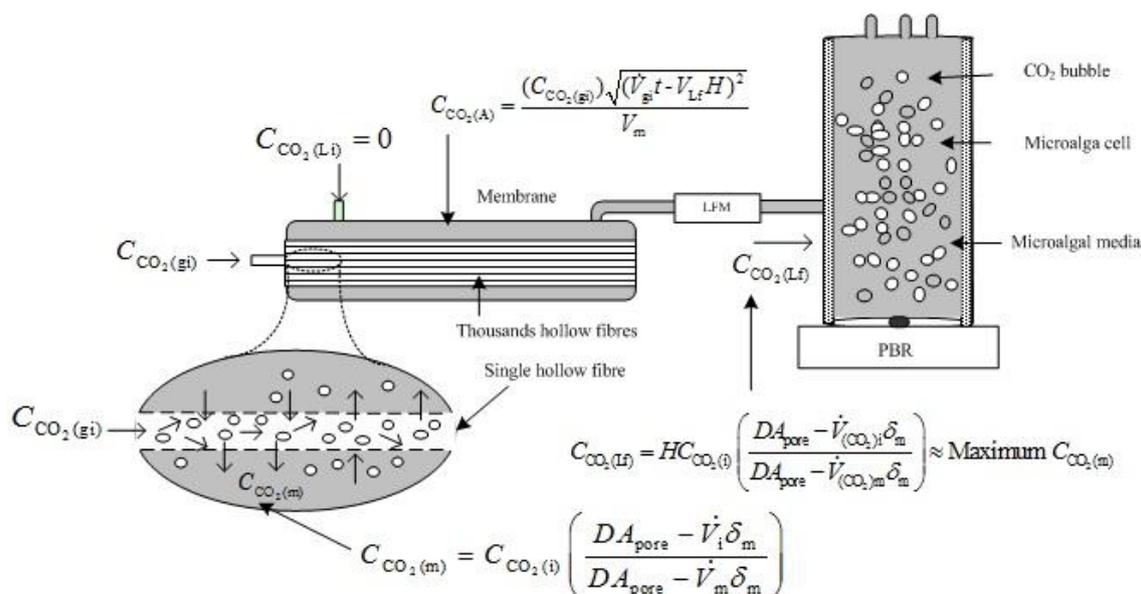


Figure 6. Compilation of proposed correlation of CO₂ feed, accumulation and solubility in microalgal media from the membrane contactor to bioreactor system.

The correlation is important to feed CO₂ into microalgal cultivation system. As discussed in previous studies, microalgae have high ability to utilise CO₂. Thus, from this correlation, optimum utilisation can be achieved and at the same time produces biomass for various purposes [28].

5. Conclusions

It was found that the diffusion coefficient of the CO₂ into the membrane pore has high impact on the gas transfer from the gas to liquid phase in the membrane. The standard deviation and the percentage error of the governed correlation compared to the experimental work is less than 20%. This value is acceptable to predict the DCO₂ by taking consideration on circumstances and equipments that were used to validate the correlation. However, the correlation was only evaluated based on microalgal media at 0.0401 kg/m³. Other experimental series is required before the correlation can be applied to other media besides microalgal media.

6. References

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