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An Effective Device for Gas–Liquid Oxygen Removal in Enclosed Microalgae Culture

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Abstract A high-performance gas–liquid transmission device (HPTD) was described in this paper. To investigate the HPTD mass transfer characteristics, the overall volumetric mass transfer coefficients, K^{A}_{La,CO_2} for the absorption of gaseous CO_2 and K^{D}_{La,O_2} for the desorption of dissolved O_2 were determined, respectively, by titration and dissolved oxygen electrode. The mass transfer capability of carbon dioxide was compared with that of dissolved oxygen in the device, and the operating conditions were optimized to suit for the large-scale enclosed micro-algae cultivation. Based on the effectiveness evaluation of the HPTD applied in one enclosed flat plate *Spirulina* culture system, it was confirmed that the HPTD can satisfy the demand of the enclosed system for carbon supplement and excessive oxygen removal.

Keywords Micro-algae · Enclosed photo-bioreactor · Volumetric transfer coefficient · Retention time · Lag time

Introduction

Micro-algae, which use solar light as their main energy source with the potential for high productivity, are tolerant to alterations in environmental conditions. Besides great values in medical care, nourishment fields, micro-algae have a great potential in the production of biodiesel for their richness in lipids, and some algae can also produce hydrogen. Micro-algae have recently been considered as a promising resource to produce renewable energy.

Micro-algae were normally cultivated in open raceway or tanks using natural or artificial light [1], which required large cultivation areas and suffered from various disadvantages,

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including difficulties in controlling cultivation conditions, evaporation of the cultivation medium, and reduction of light intensity with the increased depth of culture medium. An alternative was the enclosed cultivation that can effectively solve the above-mentioned problems. However, oxygen built-up in culture medium was generally one of the greatest constraints for enclosed micro-algae culture [2], and dissolved oxygen levels equivalent to four to five times air saturation were easily reached, which could lead to severe inhibition for algal growth [3]. Therefore, it was necessary to remove the excessively high dissolved oxygen accumulated in the culture medium. Many designs employed for the dissolved oxygen removal have been reported [4–7]; however, their mass transfer characteristics of dissolved oxygen were not explored further. A high-performance gas–liquid transmission device (HPTD) was designed and constructed in our laboratory [8]. This device can be applied in the outdoor micro-algae culture to supply the carbon dioxide for fulfilling the need of cell growth (unpublished), and it can also be employed as a gas–liquid mass transfer unit in enclosed culture mode such as flat plate photo-bioreactor system. In this system, the culture fluid coming from photosynthesis unit flowed into the device from one end and flowed out from its other end, driven by pump. Thus, carbon dioxide was supplied, and excessive dissolved oxygen in the solution was removed in the meantime.

To investigate the device's effectiveness when applying it in the enclosed micro-algae culture, studies were carried out to explore its mass transfer capability of carbon dioxide and dissolved oxygen, and the operating conditions were optimized to adapt the enclosed cultivation of micro-algae.

Materials and Methods

HPTD and Experiment Description

A schematic diagram of the HPTD was shown in Fig. 1. The device made of Perspex was constituted of clapboard, trap absorber, and gas distributor. The configuration of the trap absorber was approximately rectangular, with dimensions of 100×40×20 cm. The clapboard was inserted vertically in the middle of the trap absorber; thus, the device was divided into two regions. A gap was left between clapboard and trap absorber's bottom and could be adjusted according to the requirement. Fluid driven by pump flowed along the clapboard's two sides with reverse directions. Four gas distributors were posited in proportional spacing on the absorber's bottom in one side of the clapboard. The distributor was made of glass sand core with 30-μm hole.

Figure 2 shows the diagrammatic sketch of the experiment facility for carbon dioxide absorption and dissolved oxygen removal. The sodium carbonate and sodium acid carbonate solution with proper concentration were put into the gas–liquid transmission device and circulated driven by the pump. Gas CO_2 was aerated into the device for examining the absorption of gas CO_2. The solution sample was taken at certain time interval and titrated to determine its total carbon concentration C_T. On the condition that the liquid volumetric mass transfer coefficient K^D_{La,O_2} of dissolved oxygen was to be determined, the dissolved oxygen electrode was put into the center of the device and paralleled with liquid fluid direction, and air was aerated into the device until the solution was saturated; gas N_2 was aerated subsequently. The dissolved O_2 concentration was recorded along with experiment time.

In consideration of the amount of carbon dioxide needed in actual algae culture and the viewpoint [9] that gas–liquid mixing in airlift devices was of little importance for the mass transfer coefficient measurement, pure gaseous CO_2 was supplied to the solution with an

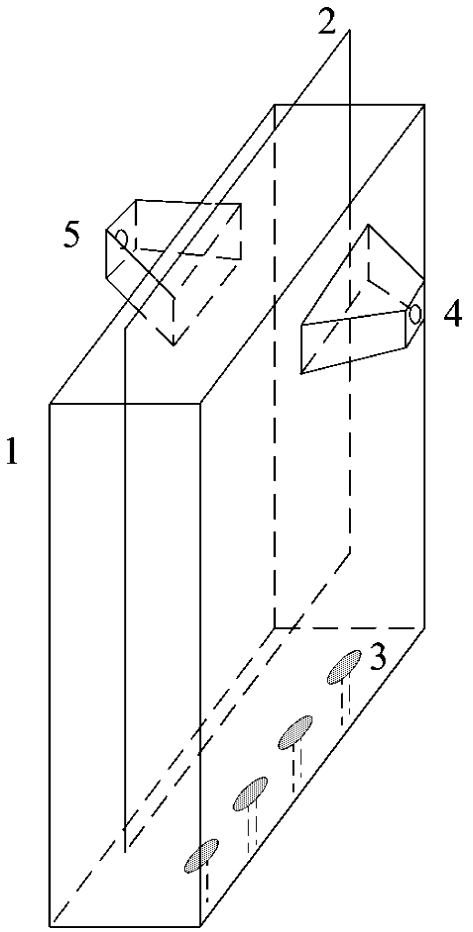

Fig. 1 Schematic diagram of the high-performance gas–liquid transmission device (HPTD). *1* Trap absorber(100×40×20 mm), *2* clapboard(100×40 mm), *3* gas distributor (diameter, 30 mm; hole, 30 μm), *4* outflow (diameter, 25 mm), *5* inflow (diameter, 25 mm)

aeration rate of 0.0035, 0.0096, 0.0181, and 0.0255 vvm (calculated by the total volume 75 l) to determine the relationship between K^{A}_{La,CO_2} and aeration rate, which was lower than the nitrogen aeration rate (0.0133, 0.0267, 0.0533, 0.0800, and 0.1067 vvm) used to determine K^{D}_{La,O_2}. The total concentration of carbon in the solution influenced little the determination of mass transfer, and the relative low initial total carbon concentration such as 0.02 mol l^{-1}, with the molar ratio of carbonate to bicarbonate of 4.0, was selected in order to shorten the experiment time. For the same reason, the small solution flow velocity was selected as 1.45 cm/s to gain the larger gas–liquid contacting time.

Measuring Principle of the Gaseous CO_2 Transfer Coefficient

The chemical absorption of carbon dioxide into mildly alkaline solution was a commonly employed technique for the measurement of overall volumetric mass transfer coefficient [9]. Chemical absorption of carbon dioxide by Na_2CO_3–$NaHCO_3$ solution was sufficiently slow to be useful for the determination of K_{La} value when the molar ratio of carbonate to bicarbonate was between 3 and 5, and the chemical enhancement factor was approximate

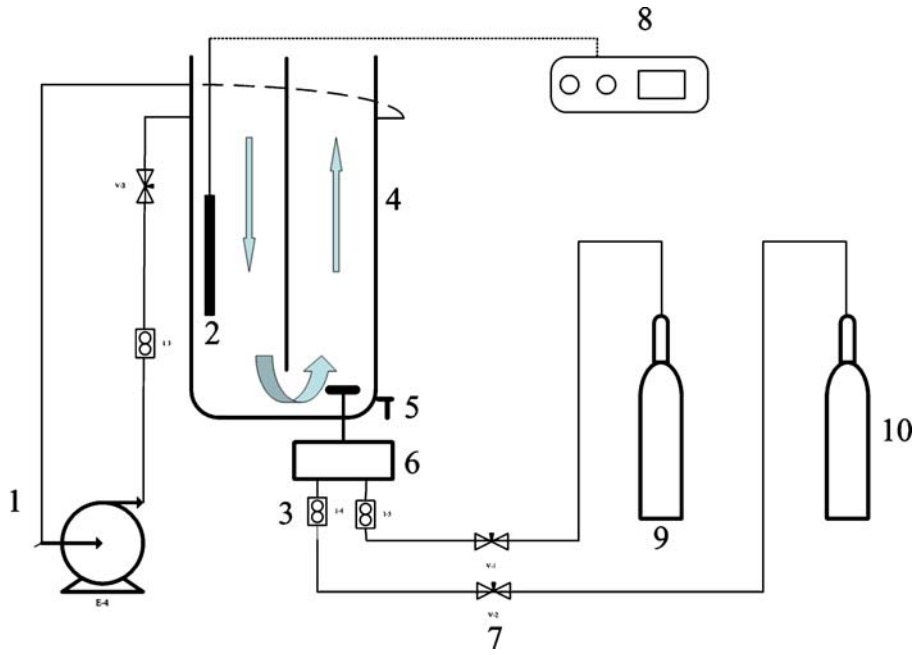

Fig. 2 Schematic diagram of the experiment facility for carbon dioxide absorption and dissolved oxygen removal. *1* Pump, *2* dissolved oxygen electrode, *3* rotor meter, *4* HPTD, *5* sample connection, *6* gas mixing tank, *7* valve, *8* measuring apparatus, *9* carbon dioxide pressure bottle, *10* air/nitrogen pressure bottle

unity [10]. When gaseous CO_2 was aerated into the alkaline solution, the following reaction occurred.

$$CO_2 + CO_3^{2-} + H_2O \rightleftharpoons 2HCO_3^-$$

The total carbon concentration was designated as the sum of the dissolved carbon dioxide CO_2 and its compounds CO_3^{2-}, HCO_3^-, and its value can be determined by titration [11]. The absorbed rate of gaseous CO_2 in the HPTD was given by:

$$\frac{dC_T}{dt} = K^A_{La,CO_2}(C_e - C_L) \quad (1)$$

where C_T was the total carbon concentration (mol l^{-1}), K^A_{La,CO_2} was overall liquid volumetric mass transfer coefficient for absorption of CO_2 (min^{-1}), C_e was CO_2 concentration in the liquid equalized with that in gas phase (mol l^{-1}), C_L was CO_2 concentration in the liquid (mol l^{-1}). When the gaseous CO_2 concentration was 100%, C_e was calculated with the following equation:

$$C_e = \frac{P}{H} \quad (2)$$

where P was the partial pressure of CO_2 (kPa), and the value of P was approximate 101.3 kPa under the experiment condition, H was Henry coefficient with the value of 2.984×10^3 kPa/

mol.l^{-1}. CO_2 in the solution was completely reacted with OH^- and H_2O, and C_L was approximate zero. Therefore, Eq. 1 was modified:

$$\frac{dC_T}{dt} = \frac{K^A_{La,CO_2} P}{H} = 0.03395 K^A_{La,CO_2} \tag{3}$$

Therefore, K^A_{La,CO_2} was determined by the curve C_T–t slope.

Measuring Principle of the Dissolved O_2 Transfer Coefficient for Desorption

Dissolved O_2 was accumulated in the culture fluid with the growth of photosynthetic cell. Therefore, excessive dissolved O_2 should be removed. The overall liquid volumetric mass transfer coefficient K^D_{La,O_2} for desorption of dissolved O_2 could be obtained by dynamic method. The dissolved O_2 concentration C_{O_2} in culture medium fell in the exponent form, and the expression was given as follow [12]:

$$\ln\left(\frac{1}{1 - E^D_{O_2}}\right) = K^D_{La,O_2} \times t \tag{4}$$

where $E^D_{O_2}$ was a fraction that showed the degree of approaching to equilibrium for O_2 desorption, and it was defined as the ratio of the mass transfer finished at any given moment $\left(C^0_{O_2} - C_{O_2}\right)$, to the maximum mass transfer $\left(C^0_{O_2} - C^f_{O_2}\right)$,

$$E^D_{O_2} = \frac{C^0_{O_2} - C_{O_2}}{C^0_{O_2} - C^f_{O_2}} \tag{5}$$

where $C^0_{O_2}$ was the initial concentration of dissolved O_2 in the liquid and $C^f_{O_2}$ was its final concentration in the liquid being desorbed.

To consider the dynamics of the electrode, relationship 4 was modified as follow [9]:

$$\ln\left(\frac{1}{1 - E^D_{O_2}}\right) = \ln\left(1 - t_E K^D_{La,O_2}\right) + K^D_{La,O_2} \times t \tag{6}$$

where t_E was the lag time of electrode. Plotting $\ln\left(\frac{1}{1-E^D_{O_2}}\right)$ against t, the straight line slope K^D_{La,O_2} was achieved, and the lag time t_E was calculated from y-intercept of the line.

Results and Discussion

Volumetric Mass Transfer Characteristics of the HPTD

Though it was possible to estimate the overall volumetric mass transfer coefficient of CO_2 from the experimentally determined overall volumetric mass transfer coefficient of O_2, for reasons of accuracy and ease in the direct relationship between them, K^A_{La,CO_2} and K^D_{La,O_2} were experimentally determined individually in this paper. Figures 3a and 4a showed the calculation examples of K^A_{La,CO_2} and K^D_{La,O_2}, and a linear relationship between mass transfer

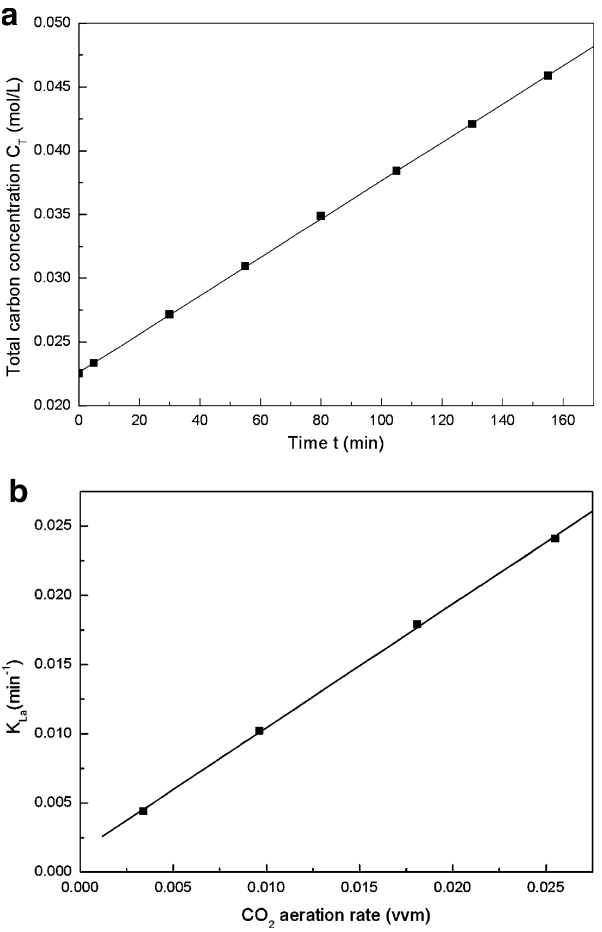

Fig. 3 **a** Variation of total carbon concentration in the liquor with absorption time. The gaseous carbon dioxide aeration rate was 0.26 l min^{-1}. $C_T = 1.503 \times 10^{-4} \times t + 0.02262$. **b** Variation of volumetric mass transfer coefficient for gaseous carbon dioxide absorption with aeration rate. $K^{A}_{La,CO_2} = 0.89255 \times Q + 0.00152$ ($0<Q<0.03$ vvm), R=0.99

coefficient and aeration rate were clearly shown individually in Figs. 3b and 4b, which showed the consistency with literature [13], and the evident linear relationship between mass transfer coefficient and aeration rate would be acquired in the condition of little aeration rate and nicer bubble size distribution.

The gas was broken into small bubbles by the gas distributor. The exterior surface of bubble formed the gas–liquid interfacial area. Carvalho and Malcata [14] indicated that gas–liquid interfacial area and fluid turbulent state were the key factors influencing the mass transfer. Specific gas–liquid interfacial area increased with the increase of gas volumetric flow rate, and their empirical correlations were described in literatures [14, 15]. The fluid turbulent intensity was strengthened when the gas flow rate increased, and the gas film and liquid film located on each side of gas–liquid interfacial surface were thinned. Therefore, the increment of the gas volumetric flow rate strengthened the mass transfer.

Another characteristic of this device was its high utilization of gas CO_2, and the maximal absorptivity 90% can be obtained (unpublished). Increasing device height can improve the gas CO_2 absorptivity due to longer retention time; however, the mass transfer coefficient decreased for bubble aggregation along with its rising. Taking the combined effects of mass

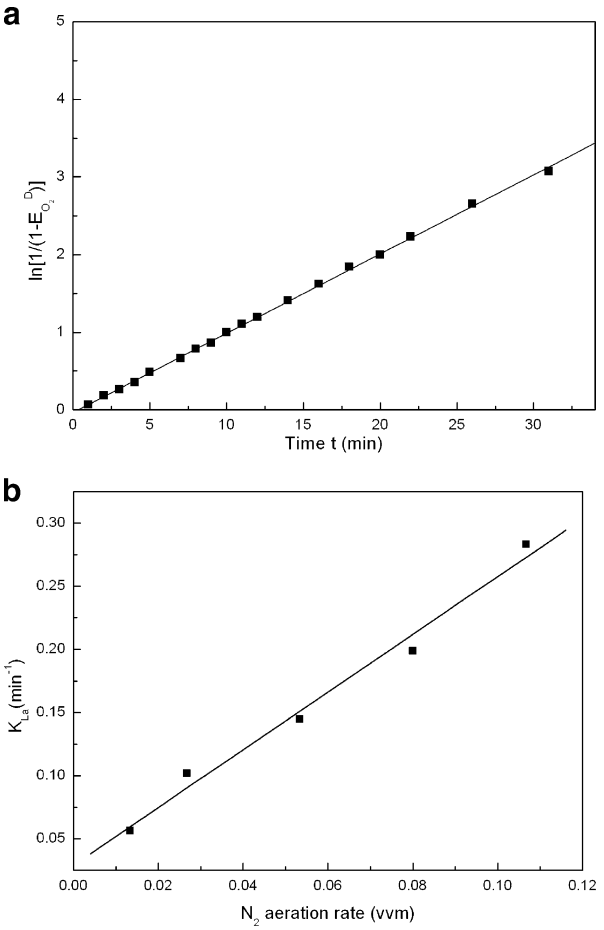

Fig. 4 **a** Variation of the expression $\ln\left(\frac{1}{1-E_{O_2}^D}\right)$ value with desorption time. The N_2 aeration rate was 2.0 l min^{-1}. $\ln\left(\frac{1}{1-E_{O_2}^D}\right) = 0.10206 \times t - 0.03171$. **b** Variation of volumetric mass transfer coefficient for dissolved oxygen desorption with aeration rate. $K_{La,O_2}^D = 2.28492 \times Q + 0.02916$ ($0 < Q < 0.12$ vvm), $R = 0.99$

transfer rate and gas absorptivity into consideration, the present design dimension of the HPTD was advisable.

Optimization of the Carbon Supplying and Dissolved Oxygen Removal Operating Conditions

The alga cell fixed CO_2 and evolved O_2 by photosynthesis with the ratio CO_2/O_2 1.0 [16]. The dissolved oxygen was easily built-up to the point inhibiting the growth of algal cell in the enclosed micro-algae culture. Therefore, it was necessary to build gas–liquid mass transfer units to remove the excessive dissolved oxygen. In this work, the above-mentioned HPTD was used as a gas–liquid mass transfer unit, and the mass transfer effectiveness was also studied. The dissolved oxygen removal rate must be higher than the carbon dioxide supplying rate to avoid the dissolved oxygen to be built up on the condition that the absorbed carbon was completely utilized by the alga cell timely. Figure 5a and b showed the mass transfer rate of the device, respectively, calculated by volumetric mass transfer coefficient and different carbon dioxide fraction in the gaseous mixture with an aeration rate

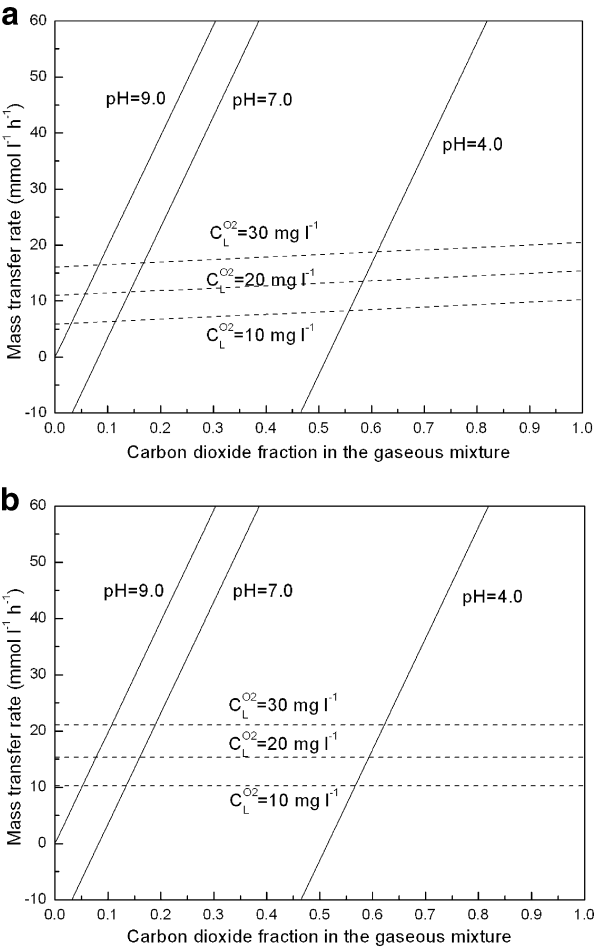

Fig. 5 **a** Mass transfer rate curve of the HPTD (gaseous mixture: CO_2 air). *Solid line* Carbon dioxide absorption rate; *broken line* dissolved oxygen desorption rate. **b** Mass transfer rate curve of the HPTD (gaseous mixture: CO_2, N_2). *Solid line* Carbon dioxide absorption rate; *broken line* dissolved oxygen desorption rate

of 0.107 vvm. The compositions of gas were CO_2 and air in Fig. 5a and CO_2 and N_2 in Fig. 5b.

According to double-film theory, gaseous carbon dioxide mass transfer rate is:

$$N_{CO_2} = K^{A}_{La,CO_2}\left(\frac{P}{H_{CO_2}}x - C_L^{CO_2}\right) \tag{9}$$

Dissolved oxygen mass transfer rate is:

$$N_{O_2} = K^{D}_{La,O_2}\left(C_L^{O_2} - \frac{P}{H_{O_2}}(1-x)q\right) \tag{10}$$

K^{A}_{La,CO_2} and K^{D}_{La,O_2} were individually 5.82 and 16.37 h^{-1} corresponding to the aeration rate 0.107 vvm, the gaseous mixture pressure was 101.325 kPa, Henry's constants H_{CO_2} and H_{O_2} were 2.984×10^3 and 7.992×10^4 kPa mol^{-1} l individually, the oxygen fraction q of the air or N_2 was assigned as 0.21 in Fig. 5a or 0.0 in Fig. 5b. Free carbon dioxide concentration in the culture medium $C_L^{CO_2}$ varied with the pH value under the condition that the total carbon concentration was constant [16], and the pH were assigned as 9.0, 7.0, and

4.0. Limiting dissolved oxygen concentration in the stationary state culture was varied with different alga species; here, $C_L^{O_2}$ were assigned as 10, 20, and 30 mg l^{-1}.

Figure 5a showed that both of mass transfer rates of carbon dioxide and dissolved oxygen increased with the increase of gaseous carbon dioxide fraction; however, the increment of carbon dioxide mass transfer rate was much higher than that of the dissolved oxygen. Decreasing the pH value of culture medium resulted in lower carbon dioxide mass transfer rate for the increase of $C_L^{CO_2}$, and higher carbon dioxide fraction in gaseous mixture was needed to ensure its adequate transfer rate. Higher $C_L^{O_2}$ resulted in higher dissolved oxygen mass transfer rate. The intersection point of two mass transfer rate lines was the point that the carbon dioxide mass transfer rate equaled to the dissolved oxygen transfer rate. With the hypothesis that the transferred carbon dioxide was completely utilized by the cell timely, the carbon dioxide fraction in gaseous mixture must be lower than that point to ensure that the dissolved oxygen evolved by the cell was not accumulated in the enclosed micro-algae steady culture.

The similar characteristics of gaseous CO_2 absorption and dissolved O_2 desorption were shown in Fig. 5b, and higher dissolved oxygen mass transfer rate was obtained due to the higher mass transfer drive for aerating pure N_2, in which the gaseous oxygen concentration was about zero. Therefore, it can effectively remove the dissolved oxygen with higher algal growing rate at the meantime; however, the shortcoming of this mode was its higher N_2 cost.

The mass transfer effectiveness of HPTD applied in one enclosed *Spirulina* sp. culture system was investigated. The optimum pH suitable to the growth of *Pavlova* sp. was about 9.0, and the limiting dissolved oxygen concentration was about 30 mg l^{-1} [17]; therefore, the carbon dioxide fraction of the gaseous mixture aerated into HPTD should be below 0.085 according to Fig. 5a. The gaseous carbon dioxide mass transfer rate, 10 mmol l^{-1} h^{-1}, was obtained with the ultimate dissolved oxygen concentration 20 mg l^{-1} when its gaseous fraction was 0.05. Assuming that alga cell constituted about 50% carbon component, the algal maximum possible productivity P maintained by carbon dioxide supplement was calculated:

$$P = \frac{10\ \text{mmol}\ \text{l}^{-1}\ \text{h}^{-1} \times 10^{-3} \times 12\ \text{g}\,\text{mol}^{-1}}{50\%} = 0.24\ \text{g}\ \text{l}^{-1}\ \text{h}^{-1}$$

The productivity could be affected by many factors such as carbon supplement, light intensity, mixing, etc, and the above productivity value was obtained under the ideal conditions. Therefore, it was higher than what had been reported [18, 19]. However, this calculated productivity value indeed showed that the HPTD not only can satisfy the demand for removing the excessive dissolved oxygen evolved by the alga cell but also can maintain high alga growth rate.

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