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Research Article

Optimization of Gas-Water Absorption Equilibrium of Carbon Dioxide for Algae Liquors: Selection of Alkaline Buffering Chemicals

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The apparent Henry's Law constant (H'), which quantifies the concentration partition of a gas-liquid equilibrium of carbon dioxide (CO_2), is used to optimize the absorption of carbon dioxide in algae liquors. The values of H' were examined under various conditions: in water at different temperatures (27 and 37°C), in alkaline buffering chemicals (sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3)), and in aquatic algae plants (*Egeria densa* and *Anubias barteri nana*). The optimal conditions for CO_2 absorption can be obtained by controlling the aqueous pH values (around weak alkalinity with pH 9-10) using sodium carbonate as an alkaline buffering chemical at 27°C, yielding exact H' values of around 16.3–21.3 atm/M, which were obtained from the mean gaseous CO_2 concentration of 803 ppm and the total aqueous carbonate concentration of 4.085 mg/L. The experimental results reveal that an alkaline buffering compound, sodium carbonate, can be added to water to maintain a constant aqueous alkalinity enough for the fixation of carbon dioxide by the photosynthesis of green algae in a photobioreactor.

1. Introduction

Carbon dioxide is the primary anthropogenic greenhouse gas, accounting for 77% of the human contribution to the greenhouse effect in recent decade [1]. Moreover, the exponential increase of carbon dioxide emissions into the atmosphere from the combustion of fossil fuels makes up the 86% of greenhouse gases [2]. The new generations of biofuels have been derived for their effective CO_2 fixation, rapid growth rate, and high capacity to produce microalgae [3]. Photosynthesis has long been recognized as a means of capturing anthropogenic carbon dioxide. Aquatic microalgae are among the fastest growing photosynthetic organisms, with carbon fixation rates that are an order of magnitude greater than those of plants on land [4]. Camacho Rubio et al. reported [5] that the minimum of 2.4×10^{-3} M carbon dioxide (approximately 106 ppm) that yields a growth rate of 0.041 h^{-1} in cultures of *Tetraselmis* can be easily maintained in a tubular photobioreactor. However, microalgal photosynthesis by 24 tested strains is sustained when the microalgae are exposed to wide concentration ranges of carbon dioxide (5.7–100%) in a flue gas [4]. Olaizola further used pH 6.5–8.5 in experiments with dissolved CO_2 concentrations over 2 orders of magnitudes (0.7–70 mg/L) and found photochemical efficiencies close to the maximum. Olaizola concluded that as long as the pH in the algae system is controlled, no deleterious effects on photochemical efficiency occur for various aqueous CO_2 contents [4]. Controlling pH in an algae system is critical for the photochemical process.

It has been developed that new solvents such as aqueous amine and piperazine promoted K_2CO_3 were applied to increase the aqueous absorption capacity of CO_2 from the flue gas [6–8]. Cullinane and Rochelle [9] measured CO_2 solubility in a wetted-wall column in 0.6–3.6 mole/L piperazine and 2.5–6.2 mole/L potassium ion at a high temperature range of 40–110°C. Rahimpour and Kashkooli [10] also simulated CO_2 solubility along with aqueous potassium ion at a high temperature range of 50–130°C. The presence of potassium

in solution increases the concentration of CO_3^{2-}/HCO_3^- in solution. Generally, the temperatures of industrial flue gas streams are lower than those for process CO_2 recovery [11]. Since studies of controlling aqueous pH in the air/algae water CO_2 system are few, in this work, various alkaline buffering compounds (sodium hydroxide and sodium carbonate) were added to water to keep its pH constant for the ordinary ambient temperatures (around 27–37°C). The apparent Henry's Law constant, which specifies the concentration partitioning relationships at the gas-liquid equilibrium for carbon dioxide, is used.

2. Method

2.1. Theory. Equations (1) and (2) describe the gas-liquid equilibrium for a carbonic system:

$$CO_{2(g)} + H_2O \longrightarrow CO_{2(aq)} + H_2O \longrightarrow H_2CO_{3(aq)} \quad (1)$$

$$H' = \frac{CO_{2(g)}}{\left(\left[CO_{2(aq)}\right] + \left[H_2CO_{3(aq)} + {HCO_3}^-_{(aq)} + {CO_3}^{2-}_{(aq)}\right]\right)}, \quad (2)$$

where H' is the apparent Henry's Law constant for the gas-liquid equilibrium of carbon dioxide. Generally, atmospheric and aqueous carbon dioxide is regarded as a closed system [12]; meaning that the mass exchange rate of carbon dioxide between the gas and liquid phases is much less than the reaction rate of carbon dioxide in water [12]. Equations (3) and (4) present main reactions of carbon dioxide in water:

$$H_2CO_{3(aq)} \overset{K_1}{\longleftrightarrow} {H^+}_{(aq)} + {HCO_3}^-_{(aq)} \quad (3)$$

$${HCO_3}^-_{(aq)} \overset{K_2}{\longleftrightarrow} {H^+}_{(aq)} + {CO_3}^{2-}_{(aq)}. \quad (4)$$

The total concentration of both diluted carbon dioxide and carbonate is denoted as a new concentration term, ${H_2CO_3}^*$, and C_T is the total concentration of aqueous carbonic species. Equation (5) is thus obtained as follows:

$$C_T = \left[{H_2CO_3}^*\right] + \left[{HCO_3}^-\right] + \left[{CO_3}^{2-}\right]. \quad (5)$$

Combining (2)–(5) yields the apparent Henry's Law constant (H') for atmospheric carbon dioxide ($CO_{2(g)}$) and C_T in

$$H' = \frac{\left[CO_{2(g)}\right]}{C_T} = \frac{\left[CO_{2(g)}\right]}{\left[{H_2CO_3}^*\right]\left[1 + K_1'/[H^+] + K_1'K_2'/[H^+]^2\right]}, \quad (6)$$

where K_1' and K_2' are ionization constants of carbonate and bicarbonate. According to Benefield et al. [12], at 25°C, dimensionless $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$. The corrected values of K_1 and K_2 at 27°C are 4.3×10^{-7} and 5.8×10^{-11} and at 37°C are 4.7×10^{-7} and 6.1×10^{-11}, respectively.

Theoretically, the value of H' for aqueous carbon dioxide is influenced by the temperature of water and other contents (i.e., pH and total dissolved solids (TDS)) [12]. Pure water that is produced using a reverse osmosis (RO) system was used as the absorption liquor, so the effect of TDS on H' can be neglected. The Results and Discussion will elucidate the effect of temperature on H'.

Gas-liquid CO_2 simulated data (Figure 2) was shown to study the effect of buffering materials NaOH and Na_2CO_3 on the values of H' in algal liquor. A total organic carbon/total inorganic carbon (TOC/TIC) analyzer was used to obtain aqueous TIC content, represented as C_T (mole/L) [13]. Simultaneously, the partial pressure (atm) of gaseous CO_2 in the headspace of the closed gas-liquid system is continuously analyzed using a CO_2 analyzer [14]. The calculated H' values can be compared to the estimated H' for various buffering materials in water, and the optimal aqueous absorption conditions of carbon dioxide can thus be obtained.

2.2. Experiment. The experiment herein was performed in three phases. In Phase I, the values of H' at the water temperatures 27 and 37°C for the absorption of 600–2000 ppm CO_2 neutral absorption water (pH ≈ 7) were compared. In Phase II, two buffering agents, NaOH and Na_2CO_3, were used to adjust the pH of the absorbent liquor around 6.5–10. In Phase III, two species of green algae were placed in the water to absorb CO_2. The effects of deviations of pH on values of H' of CO_2 during Phases I–III were observed.

2.3. Apparatus and Materials. A temperature-controlled oven (HIPOINT, 721, Taiwan) of interior volume 150-L, connected to a 0.25-Hp chilling system of controllable temperature range of 0–80°C (±0.02°C), was used. A stainless steel constant temperature basin (HIPOINT, Taiwan), which uses an LED thermal controller, provided water at a constant temperature. The visible light source to promote algal growth was fluorescent lamps (Mr. Aqua, Taiwan) with a total power of 13 W. An air agitator, connected to a flow rate regulator, provided 20 L CO_2 per min to the CO_2 aeration reactor (Figure 1). A metering pump (EYELA MP-1000H, Japan, Figure 1) transferred CO_2 enriched water at 50 mL/min into and out of a closed Erlenmeyer flask. The CO_2 equilibrium between air and water was established inside the Erlenmeyer flask. The variations of CO_2 concentration over time were examined using a CO_2 detector with a nondispersive infrared (NDIR) sensor (MultiRAE PGM-54, USA), which could detect 0–20,000 ppm CO_2, and had a resolution and response time of 10 ppm and 60 s, respectively. Aqueous TIC was investigated using a TIC/TOC analyzer (SHIMADZU, TOC-VCPH, serial number H51304400704AE, Japan). Aqueous acidity/alkalinity values were obtained using a pH meter (WTW, Germany) with a pH detection range from −2.00 to 16.00 and a pH resolution of 0.01.

Plastic syringes with a volume of 10 mL were used to extract water samples. Pure water was provided using a Millipore reverse osmosis (RO) system (RiOs-3/Milli-Q, USA). According to Serebryakova et al.'s experimental design [15], gaseous CO_2 was provided using a steel cylinder with a purity of more than 99%. All chemicals (sodium

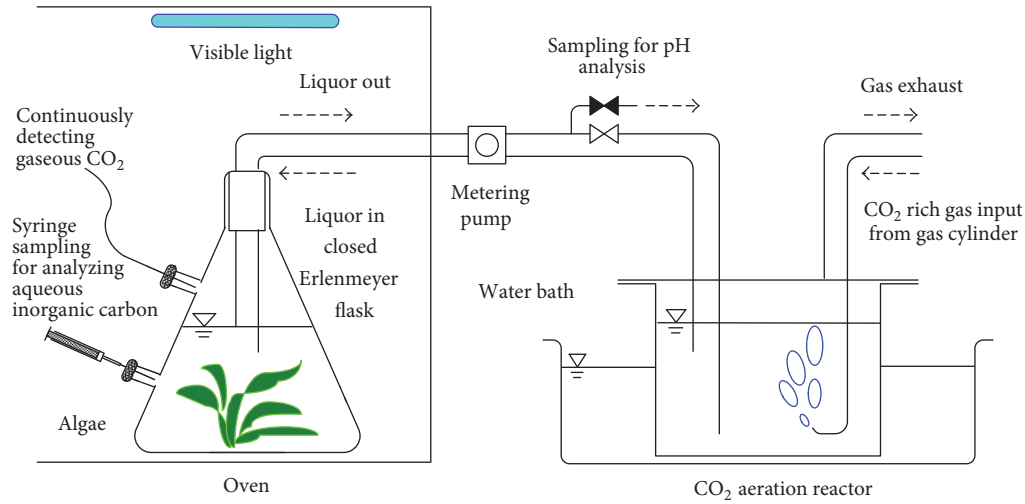


Figure 1: Experimental setup for carbon dioxide gas/liquor partitioning equilibrium.

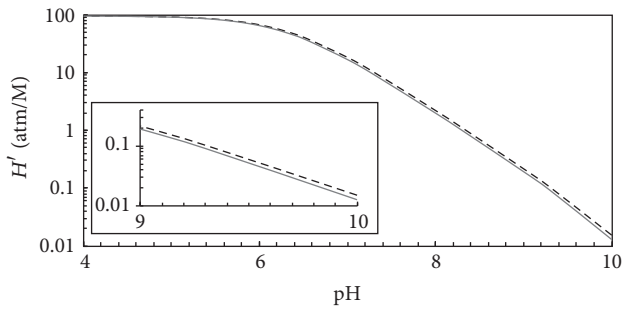


Figure 2: Variations of apparent Henry's Law constants with pH and temperature for $CO_{2(g)}$ = 1500 ppm and $H_2CO_3^*$ = 1.5 mg/L (solid line indicates 25°C and dash line indicates 35°C).

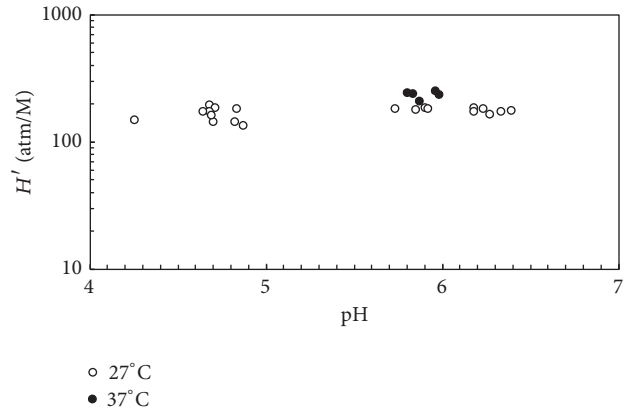


Figure 3: Variations of apparent Henry's Law constants with pH at different water temperatures.

hydroxide and sodium carbonate) were analytical grades. Two green algae, *Egeria densa* and *Anubias barteri nana*, which were approximately 10 cm tall, were purchased from a local aquarium.

3. Results and Discussion

3.1. Variation of Apparent Henry's Law Constants with pH Values

3.1.1. Theoretical Calculation. Setting CO_2 = 1,500 ppm and $H_2CO_3^*$ = 1.5 mg/L in (6) yields the variations of H' with pH at water temperature of 27 and 37°C, which are plotted in Figure 2. When the alkaline liquor (with a pH value of more than 8) absorbs 1,500 ppm CO_2, the H' values will be as low as 2.2 atm/M because of the high concentration of aqueous carbonate species, which absorb much gaseous carbon dioxide. As the pH value rises, the H' value increases; for example, at a pH in the range from 8 to 6, the H' value increases from 2.2 atm/M to 65 atm/M, so the CO_2 absorption capacity gradually falls as the pH value of the water decreases. Figure 2 further reveals that if the pH is between 4 and 5, then H' is almost in the range 90–94 atm/M, and the acidic liquor absorbs limited amount of carbon dioxide.

The H' values at 35°C and 25°C differ considerately only at pH values higher than 9 (Figure 2). The calculated H' is 0.22 atm/M at 35°C and 0.19 atm/M at 25°C at pH 9. The effect of temperature on the CO_2 gas-liquor partitioning equilibrium is much weaker than that of aqueous acidity/alkalinity.

3.1.2. Effect of Temperature on CO_2 Gas-Liquor Equilibrium in Pure Water. According to Figure 3, C_T = 0.87 ± 0.51 mg/L (which is slightly lower than the simulated concentration, 1.5 mg/L) for pH 4–7; at 27°C, the mean value of H' is 171.3 atm/M and the standard deviation is 16.8 atm/M, and at 37°C, the mean value of H' is 235.4 atm/M and the standard deviation is 30.8 atm/M. Therefore, H' and its deviations at high and low temperature reveal that the CO_2 gas-liquor equilibrium is less steady state in hot water than in cool water.

When the aqueous alkalinity at 27°C was not controlled, the pH did not fall to 7.0 or less, and H' remained in the high

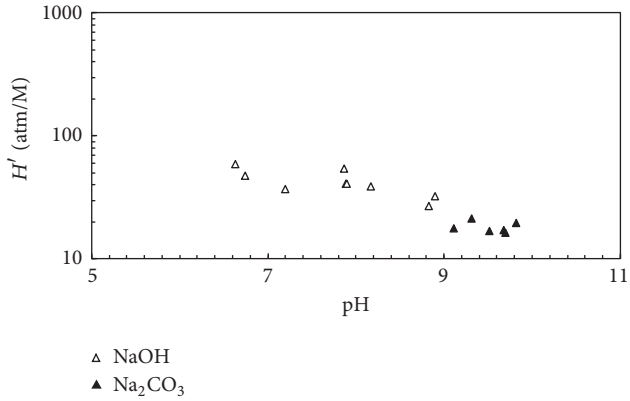


Figure 4: Variations of apparent Henry's Law constants with pH (at 27°C) for adding different alkaline buffering materials.

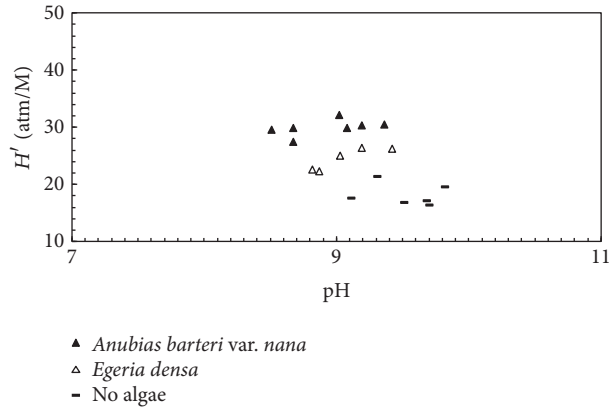


Figure 5: Variations of apparent Henry's Law constants with pH (at 27°C) for seeding different algae plants.

range of 134–185 atm/M. The values of C_T were as low as 0.87± 0.51 mg/L, so alkaline chemicals had to be added to increase the buffer capacity and dissolve more CO_2 into the water.

3.2. Effect of Alkaline Chemicals on CO_2 Partition Equilibrium. The experimental results (Figure 4) reveal that when the initial pH value of pure water ranged from 9.98 to 10.31 and the CO_2 aeration period was 2.5 h, use of NaOH as an alkaline buffer yields aqueous pH values in the range 6.6–8.9, which were much lower than the pH values (9.1–9.8) obtained using Na_2CO_3 as a buffer. Adding Na_2CO_3 yielded H' values in the range 16.3–21.3 atm/Mm whereas adding NaOH yielded H' values in the range 27.0–59.5 atm/M. Adding Na_2CO_3 yielded a mean gaseous CO_2 concentration of 803 ppm (with a standard deviation of 248 ppm) and adding NaOH yielded a mean gaseous CO_2 concentration of 1,236 ppm (with a standard deviation of 560 ppm). Briefly, the weak alkali, Na_2CO_3, had a greater acidity/alkalinity buffering capacity than the strong alkali NaOH.

3.3. Effect of Algae Plants on CO_2 Partition Equilibrium. In this phase, two green algal plants, *Egeria densa* and *Anubias barteri nana*, were seeded in the water to which Na_2CO_3 was subsequently added. The gas-liquor CO_2 partition equilibrium was then observed. According to Figure 5, the H' values in the water with algae were higher than those in water without algae: the H' value was increased by the reduction of aqueous hydrocarbonate concentration. Therefore, algae are inferred to use visible light as an energy source and aqueous hydrocarbonate as a carbon source for photosynthesis. The H' values obtained with *Anubias barteri nana* were higher than those obtained with *Egeria densa*, preliminarily indicating that the aqueous hydrocarbonate assimilation efficiency of *Anubias barteri nana* is higher than that of *Egeria densa*.

4. Conclusions

This work concerned the gas/water partitioning equilibrium of carbon dioxide under various conditions of water temperatures (27 and 37°C), alkaline buffers (NaOH and Na_2CO_3), and aquatic algae plants (*Egeria densa* and *Anubias barteri nana*). The optimal conditions for CO_2 absorption are obtained by maintaining a weakly alkaline aqueous pH of 9-10 by adding Na_2CO_3 as an alkalinity buffering chemical at 27°C; H' values were in the range 16.3–21.3 atm/M, which were obtained from mean gaseous CO_2 and aqueous $H_2CO_3^*$ concentration of 803 ppm and 4.085 mg/L, respectively.

The reduction of acidity for the carbon dioxide fixation using aquatic algae is critical to maintaining the absorption efficiency of carbon dioxide in water, and the addition of alkaline buffering chemicals seems to be a feasible means. In this work, aquatic algae plants (*Egeria densa* and *Anubias barteri nana*) were grown in carbon-dioxide-aerated and $H_2CO_3^*$-conditioned water, in which the mean aqueous $H_2CO_3^*$ concentration was 2.464 mg/L and the gaseous CO_2 concentration was 749 ppm.

Competing Interests

All authors declare they have no competing interests.

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