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Simultaneous Carbon Capture, Biomass Production, and Diary Wastewater Purification by *Spirulina maxima* Photobioreaction

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Supporting Information

ABSTRACT: The feasibility of a two-stage process involving carbon dioxide capturing and a photobioreaction (containing microalgae cells of *Spirulina maxima*) was investigated for the dual purpose of CO_2 sequestration and wastewater remediation. The study systematically demonstrated the capability of CO_2 removal through wet scrubbing using diluted wastewater as the scrubbing liquid and the potential of biomass growth in the CO_2-enriched wastewater. The NaOH-alkalized wastewater provided a CO_2 absorption capacity approximately equal to 0.5 g CO_2 g^{-1} NaOH at 0.5 M, and the absorbed CO_2 was effectively converted into usable bicarbonate to support the growth of *S. maxima*. The biomass productivity using the CO_2-enriched wastewater (30% diluted) was 0.036 g L^{-1} d^{-1}, which was in line with the productivity obtained from the controlled growth tests using $NaHCO_3$ as the carbon source. Dilution of raw dairy (milk processing) wastewater was necessary as high chemical oxygen demand (COD) loading inhibited the growth of *S. maxima*. However, with sufficient dilution, as the COD was less than 300 mg L^{-1}, the COD was effectively removed (79%) during the microalgae cultivation period, as were NH_4^+ (51%) and PO_4^- (35%) to lesser extents. The uptake of organic carbon indicated that *Spirulina* grew mixotrophically in the wastewater. Furthermore, by virtue of the hydroxide reaction with CO_2 that form aqueous carbonates (lowering the pH) and the photosynthetic activity that consumes carbonates (increase the pH), the solution pH can effectively be used as the controlling parameter in operation of the system.

1. INTRODUCTION

Emission of carbon dioxide (CO_2) as part of the postcombustion flue gases significantly contributed to the greenhouse gases (GHG) emission into the atmosphere. Capturing of CO_2 from exhausts is therefore also imperative to the GHG reduction schemes. Techniques for exhausts capturing include chemical precipitation (e.g., accelerated limestone weathering)[1] and chemical absorption (e.g., sodium hydroxide or amine solution).[2−4] CO_2 recovery is also made possible through adsorption techniques such as amine- and polyamine-based sorbents either chemically bounded[5,6] or physically adsorbed[7,8] on silica mesoporous support or carbon fibers. Membrane-based gas separation[9,10] is an attractive alternative because it is relatively energy-efficient and is potentially more selective for a given separation by taking advantage of both the solubility and diffusivity difference of the molecules to be separated.

Microbial photosynthesis, particularly by microalgae, has also gained renewed interests as a viable technology to reduce carbon emissions. The conventional open-pond cultivation takes advantage of using sunlight for photosynthetic uptake of CO_2, but suffers from the drawback of night-time respiration that emits CO_2 back to the atmosphere. The "engineered" microbial photosynthesis processes are then designed to achieve faster growth rate, higher carbon fixation efficiency, and greater growth density. These processes are also attractive because the microbial extracts may possess substantial commercial values such as dietary supplements and cosmetics components. Consequently, a number of studies involving microalgae carbon fixation have been reported.[11−13] These studies demonstrated that the microalgae (*Chlorella* sp.) had optimum growth conditions with a CO_2 concentrations in the range of 10−15%. The carbon fixation rate was in the range between 2 and 20 g L^{-1} d^{-1}.

In addition, microalgal systems have also been used for purification of wastewater including both municipal and industrial effluents.[14−16] For example, Shi et al.[17] developed a twin-layered microalgae (*Chlorella vulgaris* and *Scenedesmus rubescens*) immobilization system for treating municipal wastewater and reported extensive reduction of phosphate, ammonium, and nitrate at efficiencies well over 90% within 9 days. Li et al.[18] studied the growth of *Chlorella* sp. while using the microalgae culture to treat a highly concentrated municipal wastewater from an activated sludge process. Using continuous circulation of the microalgae culture, they reported that both autoclaved and raw wastewater supported the growth of *Chlorella* sp. with comparable growth rates, and the removal of ammonium, total nitrogen, total phosphor, and chemical organic carbon all exceeded 80% even with the high nutrients and carbon loading. Similarly, Cho et al.[19] also reported successful purification of total nitrogen (92%) and phosphor

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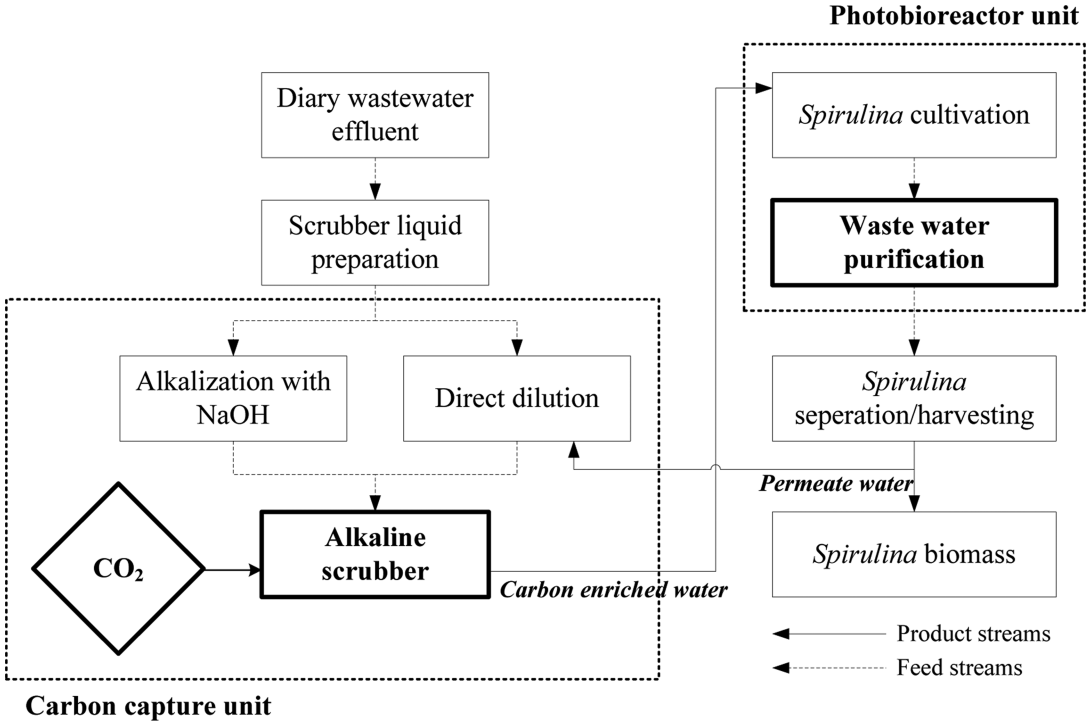

Figure 1. Integrated two-stage process (boxed with dotted lines) connecting CO_2 capture unit with photobioreactor for carbon capture, biomass production, and wastewater purification. This process takes advantages of using carbon enriched water from alkaline scrubber as carbon source for cultivation and purified wastewater as dilution solution for scrubber.

(86%) using a *Chlorella* sp.; however, they found that an appropriate bacteria-controlled pretreatment step for the wastewater through microfiltration or ultraviolet radiation was necessary to yield the highest microalgae biomass and lipid productivity. For applications in purification of industrial effluents, Yun et al.[20] studied the growth of *C. vulgaris* cultivated in wastewater discharge from a steel-making plant. CO_2 is then air bubbled (5−15% v/v) into the culture suspension. They reported successful simultaneous CO_2 fixation (26 g m^{-3} h^{-1}) and nutrients removal (0.92 g NH_3 m^{-3} h^{-1}). Lim et al.[21] found that *C. vulgaris* was able to grow in high-rate algal ponds (HRAPs) containing textile wastewater. Significant color removal (up to 50%) and nutrient reduction of NH_4−N (45%), PO_4−P (33%), and chemical oxygen demand (COD) (up to 62%) were achieved. They concluded that color was removed via cell adsorption as both Langmuir and Freundlich isotherms were followed during the biosorption study. de Gotos and co-workers[22] also evaluated the performance of HRAPs in treating 20- and 10-folds diluted swine manure at 10 days of hydraulic residence time. They reported that, under optimum environmental conditions of moderate temperatures and solar irradiances with high organic loading rates, both HRAPs supported a stable and efficient carbon and nitrogen oxidation performance, with average COD and total nitrogen removal efficiencies of 76 ± 11% and 88 ± 6%, respectively, and areal biomass productivities ranged from 21 to 28 g m^{-2} d^{-1}.

The choice of microalgae used in the above-mentioned studies mostly focused on *Chlorella* due to their ability to grow in wastewater and to consume nutrients. *Spirulina*, to a lesser extent, has also received attention as a microalgal class capable of growing in wastewater[23,24] and attaining high biomass productivity valuable as health supplements and biofuel due to their high contents of proteins and lipids.[25−27] *Spirulina* are among a number of microalgal species having shown to utilize carbon source in the form of biocarbonate (HCO_3^-) for cell growth. Many of these species contain high extracellular carboanhydrase activities responsible for the conversion of carbonate (CO_3^{2-}) to free CO_2 to facilitate CO_2 assimilation. One of these species is *Spirulina maxima*, which grows best at a high pH (9−10) and relatively high HCO_3^- concentration.[28−30] At seawater pH of 8, HCO_3^- is the predominant carbonates species, and at pH 9, about 40% is in the form of CO_3^{2-}. The utilization of HCO_3^- rather than CO_3^{2-} is important in several fronts: (i) CO_3^{2-} is poorly soluble in water and is easily precipitated as carbonate salts; (ii) control of species contamination is relatively simple since only a limited number of microalgal species favors growth in high pH and HCO_3^- concentration. The use of *Spirulina* for mass production from wastewater purification also provides distinct advantages in that its filamentous form makes harvesting easier and less costly.

The major constraints of applying *Spirulina* for wastewater purification and biomass production are the need to add HCO_3^- and alkaline agents, as well as the large wastewater dilution normally necessary for their growth. All of these factors would escalate the operating costs of the method. Hence, to make the process more economically competitive, this study proposes an alkaline absorption process for CO_2 capturing from flue gases using a diluted wastewater, followed by a photobioreactor for cultivation using the CO_2-enriched wastewater, as schematized in Figure 1. This is an integrated process of two independent types of reactors that can be operated separately or simultaneously. In this study, those two reactors were operated separately in order to facilitate the use of space. Water outlet from the photobioreactor unit was recycled back to the CO_2 capture unit as a dilution solution. Wastewater from alkaline scrubber was enriched with carbon source (CO_3^{2-} and

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HCO_3^-) and then could be directly used in *Spirulina* cultivation. By using NaOH as absorbent in the alkaline scrubber, CO_2 can be removed from air to generate organic carbon species through the overall reaction[31]

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \quad (1)$$

with the rate-determining step being

$$CO_2 + OH^- \rightarrow HCO_3^- \quad (2)$$

followed by the ionic reaction

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (3)$$

This process satisfies the need for a large-volume carbon capturing from exhausts such as postcombustion process, whereas the wastewater is reused to absorb CO_2 and to support microalgae growth. In addition, it serves as a sustainable environmental system that omits generation of waste in any forms by recycling all the usable resources (i.e., biomass and waste/purified water) within the process; thus, minimize the associated environmental impacts brought from the process. Therefore, the choice of the microalgal species (i.e., *S. maxima*) and the absorbent (NaOH) makes the combined process simple yet effective. The requirement of sole carbon source of HCO_3^- can be easily met by using NaOH to absorb CO_2 from CO_2-enriched air, which provides a strong economic incentive. Other major nutrient components (i.e., N and P) supporting biomass growth can be fully or partially provided from a waste effluent having suitable properties to be used as the scrubbing liquid. The two-stage process is also spatially flexible, as the CO_2 scrubber and the photobioreactors may be located separately.

This work investigates the carbon capturing capacity of the alkalized wastewater as well as the cell growth capability of *S. maxima* in the CO_2-enriched wastewater. Change of dosages in carbon and nitrate sources are studied in investigating the correlation between nutrient sources and biomass productivity. Meanwhile, the extent of the nutrients uptake is also examined, as they are critical determinants for the biomass productivity and water purification level.

2. MATERIAL AND METHODS

2.1. Microalgae Selection and Cultivation. *S. maxima*, a multicellular filamentous cyanobacterium with a helical shape, was obtained from Taiwan Fisheries Research Institute (Tung-Kang, Taiwan) and was used as the primary microalgae for carbon absorption and wastewater purification experiments. The cells of *S. maxima* were cultured in a modified f/2 mineral medium that includes 1.25 g $NaNO_3$, 0.6 g NH_4NO_3, 0.5 g K_2HPO_4, 1.0 g K_2SO_4, and 1.0 g NaCl per liter of medium. $NaHCO_3$ with various doses (0−16 g L^{-1}) was added as the sole carbon source in the growth study. The cultures were grown in a series of 1-L Duran borosilicate bottles (Schott Taiwan Ltd.) under room temperature and exposed to three parallel 40W fluorescent bar lamps (China Electric Co., Taiwan) continuously for 18 h, followed by 6 h in dark. The average photon flux, as measured by a quantum sensor (Apogee MQ-100, U.S.A.), was 220 μmol m^{-2} s^{-1}. Each cultivation cycle lasted 8 days, beyond which the high medium pH and the weak light penetration began interfering the cell growth. During the cultivation period, the culture suspensions were continuously aerated with filtered air (0.4 vol air/vol solution min^{-1}). The cell density was determined by optical absorbance (λ = 680 nm) using a UV−vis spectrophotometer (Jasco 4600, Japan) and was calibrated periodically with biomass dry weight (DW) measurement. The correlation between dry biomass density and optical density (OD_{680}) remained linear up to OD of 1.2:

$$g\,DW\,l^{-1} = 0.46\,OD_{680} - 0.01 \quad (n = 6;\ p < 0.01) \quad (4)$$

Light shading effect started interfering light penetration and deviated the OD linearity with DW when OD_{680} exceeded 1.2. Consequently, *S. maxima* cultures with OD_{680} exceeding 1.2 were diluted to determine their biomass. Each cultivation cycle started with an OD of approximately 0.2, which was determined to be the necessary starting cell density to yield optimum growth rate.

2.2. Alkaline CO_2 Scrubber. For the alkaline CO_2 scrubber, the absorbing liquid was a dilute NaOH solution or a dilute diary wastewater to absorb CO_2-enriched air. As shown in Figure 2, the solution was nozzle-delivered and recirculated

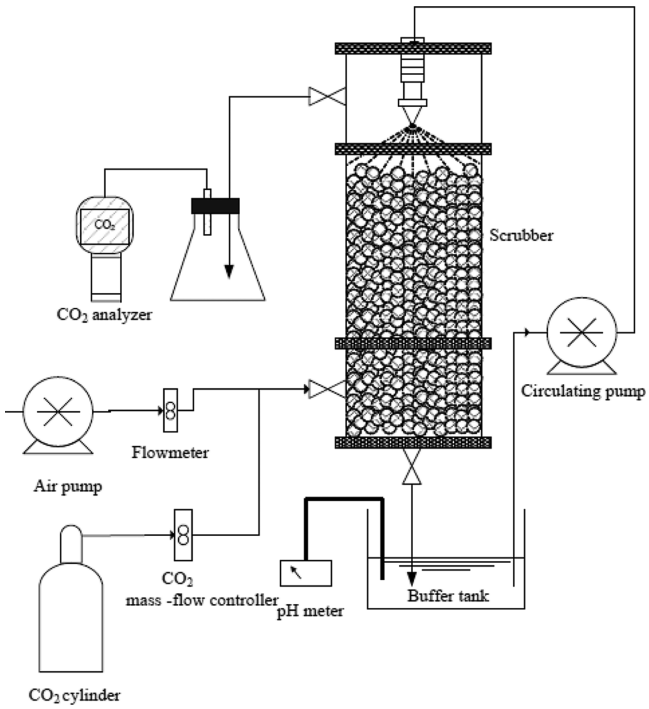

Figure 2. Schematic setup of alkaline scrubber system for CO_2 capture from air.

at a volumetric flow rate of 0.6 L min^{-1} through a packed column (packed height, 325 mm; internal diameter, 60 mm) filled with size-15 plastic pall rings (specific surface area, 210 m^2 m^{-3}; porosity, 82%). The scrubbing performance was evaluated using various air flow rates (5 to 20 L min^{-1}), NaOH concentrations (0.1 to 1.0 M), and inlet CO_2 concentrations (ambient air to 10% v/v) as detected by a portable nondispersive infrared CO_2 sensor (IAQ CALC7515, TSI, USA). Both clean water produced from reverse osmosis (RO) membrane and dilute wastewater (30% dilution) were tested as the absorbing liquids. For elevated CO_2 absorption tests, pure CO_2 from a certified gas cylinder was mixed with filtered air to obtain target CO_2 concentrations. The CO_2 outlet concentration was directly detected by the sensor and recorded at two-minute intervals.

The average CO_2 uptake rate (J_{CO2}) for the absorption studies was determined on the basis of the largest CO_2

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concentration difference ($\Delta[CO_2]_{max}$ in μmol L^{-1}) between the inlet (i.e., ambient condition) and the outlet, using the following equation:

$$J_{CO_2} = \frac{(\Delta[CO_2]_{max})(L)}{A_w} \quad (5)$$

where L denotes the alkaline liquid recirculation flow rate (in L s^{-1}), and A_w is the wetted surface area (m^2) of the packing material. The absorption capacity at complete saturation for these tests was not determined as the experimental runs were terminated before complete saturation occurred. Conversely, for absorption studies involving elevated CO_2 concentration, the saturation time was evidently shorter than that in ambient condition. Therefore, the CO_2 absorption capacity (θ) was evaluated by

$$\theta = \frac{\int_0^{t_{Saturation}} G(\Delta[CO_2])\, dt}{M_{NaOH}} \quad (6)$$

where G represents the air flow rate, $t_{Saturation}$ is the time taken to reach complete saturation, ($\Delta[CO_2]$) is the CO_2 concentration difference between the inlet and the outlet, and M_{NaOH} denotes the NaOH dosage in mass basis given a fixed volume of absorption liquid. In these experiments, the CO_2 uptake rate were not determined because partial saturation (CO_2 breakthrough) occurred within seconds after the experiments started, preventing accurate determination of the rate of uptake.

In addition to the monitoring of CO_2 concentrations, total inorganic carbon (TIC) dissolved and accumulated in the solution was also measured by a total organic carbon (TOC) analyzer (Elementar Liqui TOC, U.S.A.). The TIC was calculated as the difference between the total carbon (TC) and TOC. The calibration test demonstrated that TIC was linearly correlated (TIC = 0.107 [$NaHCO_3$], r^2 = 0.998) with $NaHCO_{3(aq)}$ in the range of 0 to 16 g L^{-1}.

2.3. Wastewater Characteristics. The experimental wastewater was obtained from the milk processing factory at Tunghai University, Taiwan. The water characteristics were determined following the Standard Methods,[32] including the phenate method for ammonia (SM 4500-NH_3-G), the ascorbic acid method for phosphates (SM 4500-P-E), and the cadmium reduction method for nitrate (SM 4500-NO_3-B). The COD was determined by the dichromate colorimetric method. These parameters were analyzed colorimetrically using a Hach 1000 spectrophotometer. Additionally, the five-day biochemical oxygen demand (BOD_5) was determined by following SM 5210B. Water quality parameters for the milk processing wastewater were determined as the following: BOD_5 = 608 mg L^{-1}, COD = 1064 mg L^{-1}, [NH_4^+] = 75 mg L^{-1}, [NO_3^-] = 48 mg L^{-1}, and [PO_4^{3-}] = 322 mg L^{-1}. The wastewater was autoclaved and subsequently diluted by the ratio of 90% (e.g., 900 mL wastewater and 100 mL RO water in 1-L solution), 70%, 50%, 30%, 10%, and 5% (with 5% being the most dilute sample) for cultivation of *S. maxima*. The residual contents of organic carbon and nutrients (NH_4–N, NO_3–N, PO_4–P) were determined after the termination of cultivation.

3. RESULTS AND DISCUSSION

3.1. Growth Characteristics of *S. maxima* in Controlled Conditions. The specific growth rates of *S. maxima* and its volumetric productivity (dry biomass weights) cultivated under various photoautotrophic growth conditions are shown in Table S1 (Supporting Information). Sodium bicarbonate ($NaHCO_3$), dosage ranges from blank progressively to 16 g L^{-1}, was added to the medium as the carbon source, and ammonium nitrate (NH_4NO_3) was added as the nitrogen source. The pH of the medium slightly increased as greater dosage of $NaHCO_3$ was added, topping at about 10.1 with a dosage of 16 g L^{-1}. No cell growth was observed for the sample without $NaHCO_3$.

Both the volumetric productivity and the specific growth rates of *S. maxima* increased with increasing dosage of $NaHCO_3$, while NH_4NO_3 was under a fixed dosage. The light intensity applied in the growth condition was similar to that used in Vonshak's study,[33] as they reported that the growth of *S. platensis* became saturated at the range 150–200 μmol m^{-2} s^{-1}. It is noted that, since this range of light flux represents only a minor portion of the total solar radiance at the visible spectrum, cultures generally grow significantly better in the outdoor environments. In this study, though the greatest dosage of $NaHCO_3$ supplied for growth was 16 g L^{-1}, one can still observe that the biomass was still markedly increasing; significantly higher biomass production and specific growth rate were expected if greater $NaHCO_3$ dosages were supplied. Additionally, the extent of carbon utilization was measured by the average consumption rate of TIC, and the TIC consumption rates were positively correlated with the biomass productivity.

Growth conditions with various NH_4NO_3 dosages indicated that type and concentration of nitrogen sources were also critical to the growth of *Spirulina*. Nitrate (NO_3^-) was not assimilated, as NO_3^- concentration was essentially unchanged during all of the growth tests. Contrarily, no cell growth was observed when NH_4^+ was either absent or overdosed at 0.9 g L^{-1}. The *Spirulina* showed similar growth characteristics when added with 0.3 g L^{-1} or 0.6 g L^{-1} NH^{4+}, with the latter showing moderately higher extent of specific growth rate (0.496 d^{-1}) and mean NH_4^+ consumption rate of 17.6 g L^{-1} d^{-1}.

The elemental analysis for *S. maxima* cultivated on mineral medium resulted in the following composition (% atomic dry weight): C, 44.8%; N, 5.8%; O, 36.5%; and H, 6.8%. Under the condition that yielded the highest biomass productivity ($NaHCO_3$ dosage of 16 g L^{-1} and a NH_4NO_3 dosage of 0.6 g L^{-1} at pH 9), the estimated overall carbon conversion ratio to *S. maxima* cell biomass was 13.5%, basing on the cell carbon content of 0.448 g C g^{-1} cell. However, the condition with the greatest carbon conversion occurred when the $NaHCO_3$ dosage was 4 g L^{-1} (conversion ratio, 27.3%). Several studies have indicated that not all the CO_2 assimilation could be converted to cellular biomass. For instance, in the study of Jacob-Lopes et al. (2010),[34] the cultivation of *Aphanothece microscopic Nageli* in refinery wastewater only revealed 5.6% of the CO_2 conversion into biomass, a result similar to those accounted by Chiu et al. (2008)[12] in attempt to use *Chlorella* for fixing 15% CO_2. Sydney et al. (2010)[34] also estimated that about 20% of the carbon retained in their photobioreactor system was not incorporated into *S. platansis* cells. There appeared to be potential physicochemical routes (e.g., precipitation of CO_3^{2-} and/or HCO_3^-) and biological routes (production of biopolymers and volatile hydrocarbons) that account for a bulk of the CO_2 retained in the cultivation systems. It is also worth noting that, since the solution pH approached the equilibrium point (pK = 10.3) between HCO_3^- and CO_3^{2-} species and carbon source in the form of CO_3^{2-} was not used as

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for cell photosynthesis, the actual carbon (HCO_3^-) incorporated into biomass was estimated to be about 22% at pH 9.

As shown in Figure 3, the carbon-to-nitrogen ratio was apparently a controlling factor for the carbon conversion ratio.

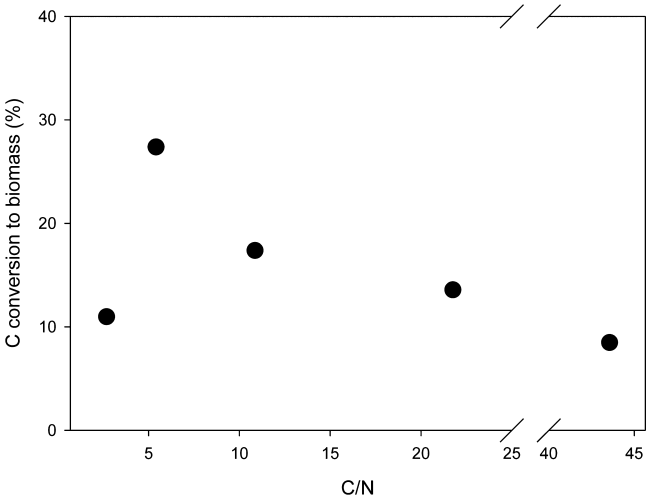

Figure 3. Carbon conversion rate to biomass as a function of C/N in the growth study.

For example, at $NaHCO_3$ dosage of 4 g L^{-1} and NH_4NO_3 dosage of 0.6 g L^{-1}, the C/N ratio was 5.5, representing a slightly nitrogen-rich condition favoring cell synthesis as supposed to conditions where nitrogen-deficit occurred. For the cultivation study using CO_2-enriched RO water, the carbon conversion ratio (57%) to cell biomass was higher for the condition with 0.1 M NaOH to absorb 10% CO_2 and augmented with 0.6 g L^{-1} NH_4^+, as compared with the condition using 0.5 M NaOH (conversion ratio of 22.1%). Given that the C/N ratio contained in the CO_2-enriched solution was 5.85 for the former and 26.4 for the latter, one can observe that nitrogen was the limiting factor controlling the carbon conversion ratio.

3.2. Growth of *S. maxima* Using Wastewater Augmented with $NaHCO_3$. The growth characteristics of *S. maxima* using dilute wastewater as the growth medium were evaluated. As mentioned previously, these experiments were conducted by diluting the raw wastewater with RO water at various dilution factors. After dilution, only $NaHCO_3$ (16 g L^{-1}) was added to the solution to provide the necessary base of comparison with those cultivated in pure water.

The growth experiments showed that *S. maxima* did not grow on wastewater with dilution factors of 90%, 70%, and 50%. Since the tested wastewater did not contain toxic compounds such as heavy metals and recalcitrant industrial organic chemicals, the high organic carbon loading (BOD and COD) was likely to be the cause of growth inhibition. In the present study, samples with dilution factors less than 30% led to COD concentrations less than 300 mg L^{-1}, which resulted in significant growth of *S. maxima*. The specific growth rates using wastewater dilution at 30% and 10% were comparable, having difference less than 3% (in duplicates) at an average of 0.29 d^{-1} and 0.28 d^{-1}, respectively. These specific growth rates were in the same order of magnitude, though somewhat lower, as compared to those reported in Table S1 (Supporting Information). It must be noted that, while the added $NaHCO_3$ dosage were identical for these studies, the nitrogen contents (NH_4^+) in the dilute wastewater solutions were at least an order of magnitude lesser. Furthermore, the growth rate at 5% dilution factor was markedly lower (0.12 d^{-1}), suggesting that an optimum dilution is expected to provide a suitable range of nutrients to cell growth. As a result, it was recommended that the wastewater for the carbon capturing and microalgae cultivation tests was diluted at 30%.

The chemical composition analysis of *S. maxima* grown on 30% diluted wastewater were crude protein, 65.2%; carbohydrates, 11.3%; total lipids, 7.0%; chlorophyll, 3.2%; and ash, 6.8%. For a comparison, those components for the cells grown on the mineral medium (containing 16 g L^{-1} $NaHCO_3$) in the same order were 72.5%, 8.3%, 6.3%, 4.8%, and 5.2%, respectively. The higher crude protein and pigment contents under nitrogen-sufficient conditions were consistent with those reported by Gordillo et al. (1999).[35] Also, the cells grown on diluted wastewater, where nitrogen was limited, contained greater carbohydrate content. Apparently, nitrogen limitation caused photoassimilated carbon to be redirected toward the synthesis of carbohydrates instead of proteins and chlorophyll.[35,36]

3.3. CO_2 Absorbing Capacity of Alkaline Scrubber with RO- and Wastewater as Absorbing Media. The CO_2 absorption tests were performed by dosing various NaOH quantities into RO water and 30% diluted wastewater. Figure 4

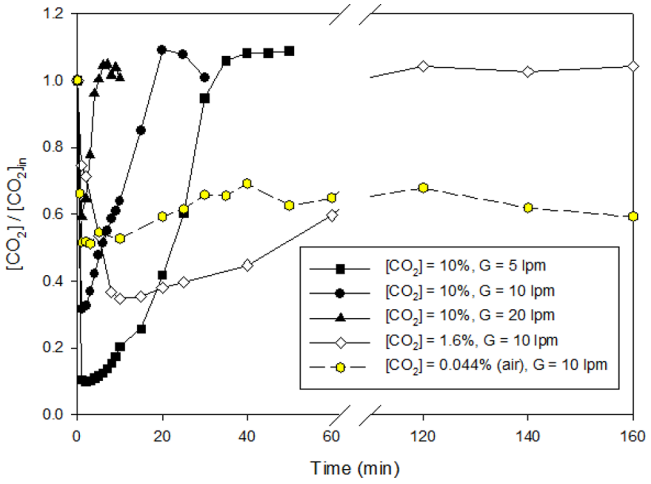

Figure 4. Alkaline scrubber breakthroughs of CO_2 under various tested conditions (L = 0.6 L min^{-1}, [NaOH] = 0.1M).

shows a set of selected profiles of the normalized CO_2 concentration as a function of scrubbing time with identical NaOH dosage (0.1 M) but various feed CO_2 concentrations and gas flow rates. One can readily note that, for the absorption of CO_2 from ambient air (440 ppmv or 0.044%) at an air flow rate of 10 L min^{-1}, the CO_2 concentration immediately reduced and remained relatively constant for the duration of the absorption experiment. Similar results were obtained for other absorption experiments using air as the feed gas under different flow rates. The extent of CO_2 absorption, however, increased with decreasing gas flow rate and increasing in NaOH dosage. For example, with an air flow rate of 20 L min^{-1}, the CO_2 capturing efficiency from ambient air increased from 35% at a NaOH dosage of 0.1 M to 50% (at 0.5 M), and further to 65% (at 1.0 M). Similarly, with a NaOH dosage of 1.0 M, the CO_2 capturing efficiency drastically improved from 65% at a flow

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rate of 20 L min^{-1} to near 100% as the air flow rate was reduced to 5 L min^{-1}.

In contrast to the "flat" profiles for the CO_2 absorption experiments from ambient air, gradual CO_2 breakthrough occurred as the CO_2 concentration in air was increased from 1.6% to 10% (Figure 4). It is also noted that, with an increase in gas flow rate, not only the duration of complete breakthrough was shortened, but the CO_2 reduction at its largest extent also decreased. The distinct CO_2 concentration profiles led to a different approach to quantify the degree of the CO_2 absorption, namely the average absorption rate (eq 5) from ambient air, and the absorption capacity (eq 6) from CO_2-enriched air. These results are summarized in Table S2 (Supporting Information).

In an alkaline scrubber, CO_2 is absorbed by the NaOH alkaline solution to produce dissolved $NaHCO_3$, which may be further converted to sodium carbonate (Na_2CO_3). CO_3^{2-} is considered as the predominant carbon species at the initial stage of CO_2 absorption, as the pH of the NaOH dosed solution exceeded the pH of the second equilibrium point (i.e., pK_2 = 10.3). As the hydroxyl ions gradually deplete and the solution pH drops, HCO_3^- becomes a more abundant carbon species.

For the absorption of CO_2 in ambient air performed in this study, Table S2 in the Supporting Information shows that the lowest value of the average CO_2 uptake rate (J_{CO_2}) was 0.296 μmol m^{-2} s^{-1} under a gas flow rate of 20 L min^{-1} and a NaOH dosage of 0.1 M. As presented earlier, the uptake flux increased with reducing gas flow rate and increasing NaOH dosage, reaching as high as 0.801 μmol m^{-2} s^{-1} when the air flow rate was 5 L min^{-1}. In the case of abundant supply of [OH^-] to react with CO_2, the reaction rate follows the first-order absorption with the following expression (i.e., the flux into solution is proportional to CO_2 concentration in the gas phase):[37]

$$J_{CO_2} = \sqrt{D_L k_d [OH^-]}\, K_H p_{CO_2} \quad (7)$$

where D_L is referred to as the CO_2 diffusivity in NaOH (1.78×10^{-9} m^2 s^{-1} in room temperature), k_d as the kinetic constant (6745 L mol^{-1} s^{-1}), K_H as the Henry's law constant (0.79), and p_{CO_2} as the CO_2 concentration (mol m^{-3}) in air. For absorption of CO_2 in ambient air, Zeman[38] estimated from eq 7 that the maximum J_{CO_2} at approximately 30 μmol m^{-2} s^{-1}, assuming a 50% capture rate and 380 ppmv (0.015 mol m^{-3}) CO_2 concentration in air into a 1 molar NaOH solution; even a cumulative flux of 20 μmol m^{-2} s^{-1} could be expected nearing complete conversion of OH^- to CO_3^{2-}. These values are 2 orders of magnitude greater than those calculated in this study and are approached only when much higher CO_2 concentration in air occurs. One notes that the first-order kinetics still holds true since the latter concentration (i.e., 1.6% into 0.1 M NaOH) was also two-orders of magnitude greater than the ambient CO_2 concentration (i.e, ~0.04% into 0.1 M NaOH). Therefore, the discrepancies of the fluxes between the experimental results from this work and those from eq 5 are likely attributable to the kinetic constant, which was an empirically derived function of the ionic strength. For extraction of CO_2 from air, the presence of low CO_2 concentration suggests that air-side transport resistance dominated by the diffusion barrier in the boundary layer becomes important, as substantiated by the strong effect of gas flow rate to the CO_2 uptake rate. Consequently, the kinetics of the overall reaction deviates from the conditions used for deriving the kinetic constant in eq 3.

Figure 5 shows the total dissolved TIC concentration in the absorbing solution as a function of absorption time for CO_2 absorption from ambient air. The primary feature of these results was the linear increase of TIC concentration with CO_2 absorption time, with the slopes representing the rate of TIC accumulation. This linear increase of TIC, all occurred at pH greater than 8.5, showed that the rate of CO_2 absorption remained constant even when the pH gradually reduced due to the continuing spending of hydroxyl ions in the reaction of dissolved CO_2. Additionally, for the CO_2 absorption from ambient air, one also notes that an air flow rate of 10 L min^{-1} yielded the highest rate of TIC accumulation as compared to either 5 L min^{-1} or 20 L min^{-1}, even though J_{CO_2} at 5 L min^{-1} was higher than that at 10 L min^{-1}. This result suggests that, in practice, there exists an optimum air flow rate (or air-to-liquid flow ratio) for a given CO_2 concentration and liquid flow rate, to attain the highest rate of CO_2 absorption in the scrubbing liquid; this optimum air flow rate may be different from the one that gives rise to the highest CO_2 absorption efficiency.

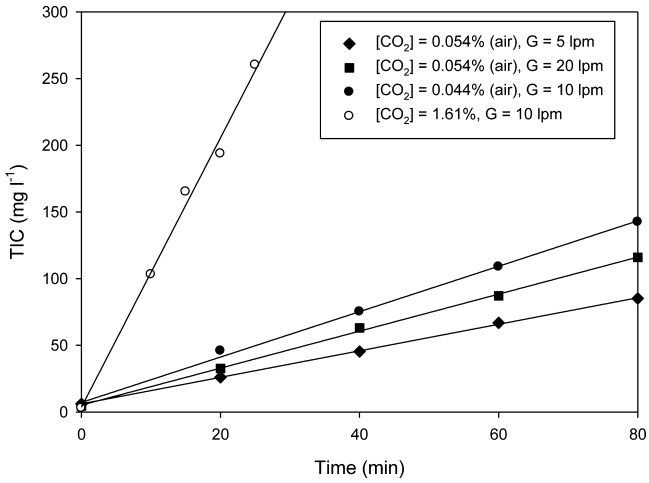

Figure 5. Dissolved inorganic carbon concentration as a function of absorption time during alkaline scrubber of air samples.

The absorption capacity determined from the CO_2 scrubbing experiments with elevated CO_2 concentrations ranged from 0.44 gCO_2 g^{-1} NaOH to 2.13 gCO_2 g^{-1} NaOH, as shown in Table S2 (Supporting Information). The absorptivity increased with reducing air flow rates but did not noticeably vary with hydroxide (OH^-) concentration because the OH^- were depleted rapidly such that the process became reaction-limited rather than diffusion-limited, as was the case in ambient CO_2 absorption. Table S2 (Supporting Inforamtion) also shows that, using the NaOH-dosed dilute wastewater, the CO_2 absorptivity was only marginally reduced as compared with those using RO water as the scrubbing liquid. These values are comparable to the absorption capacity of aqueous ammonia processes such as monoethanolamine (MEA) at 0.4 g CO_2 g^{-1} MEA and of ammonia (NH_3) at 1.2 g CO_2 g^{-1} NH_3.[39,40] Therefore, without considering other secondary factors (e.g., corrosion problems, solvent regeneration or byproduct reuse value, cocapturing of multiple flue gas components), CO_2 capturing by alkaline absorption offers a simple yet competitive process that can be further applied for microalgae cultivation.

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As opposed to the linear rate of TIC accumulation in the case of CO_2 absorption from ambient air, the rate of TIC accumulation markedly decreased with time when high CO_2 concentrations were experimented, as shown in Figure 6 using

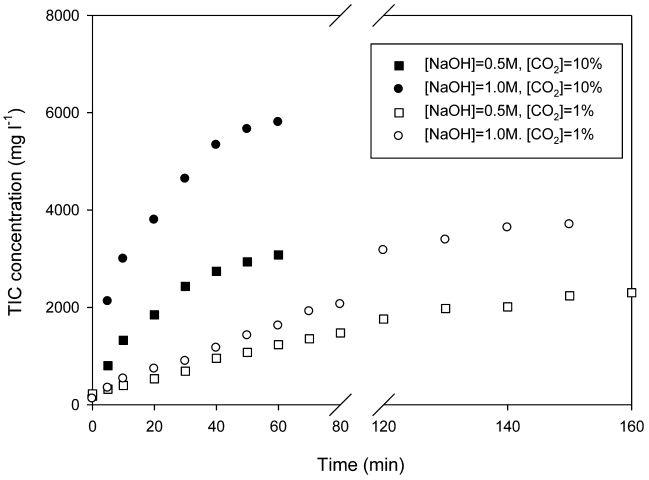

Figure 6. Dissolved inorganic carbon concentration as a function of absorption time during alkaline scrubber of enriched CO_2 air samples (1% v/v and 10% v/v) using 30% dilute wastewater as the scrubber medium.

dilute wastewater as an example. These results were clearly caused by the gradual depletion of OH^- and strongly varied with the CO_2 concentration in air. For a tested CO_2 concentration of 1% v/v, saturation (i.e., TIC concentration essentially ceased to increase with time) occurred about 2 h, whereas those for 10% v/v occurred about 1 h. One also notes the increased NaOH dosage clearly led to a higher rate of TIC accumulation in the solution but did not significantly prolong the absorption duration to reach saturation.

The reactions associated with alkaline scrubbing of CO_2 from air carry important implication to microalgae growth using the CO_2-captured solution as the growth medium, since most of the microalgae species such as *Spirulina* only grow on HCO_3^-. Though the absorption flux calculated from this study using a typical bench-scale packed-bed scrubber was substantially lower than those reported in literatures, the absorption capacity appeared to be competitive with other liquid-based CO_2 capturing processes. Decoupling of the CO_2 capturing (absorption) system from the microalgae cultivation system allows for design and operating flexibility when implementing the process in spatially limited sites (e.g., roof of a building). Additionally, one may also use the solution pH as the control parameter for CO_2 capturing in practice. For example, in a pilot-scale study, Den et al.[41] set a pH of 8.5 as the end-point of the CO_2 absorption process using 0.1 M NaOH solution. This pH would suit the growth condition of *Spirulina* and ensure the availability of HCO_3^- as the carbon source for photosynthetic growth.

3.4. Growth of *S. maxima* and Nutrient Uptake Using CO_2-Enriched Dilute Wastewater. The growth characteristics of *S. maxima* using the dilute wastewater as the CO_2-absorbing media were evaluated. These tests were conducted by dosing the 30%-diluted wastewater with 0.5 M NaOH for CO_2 absorption from air containing 10% v/v CO_2. Other growth conditions were identical to those reported in the *S. maxima* growth sections.

To establish a basis for comparison, RO-water containing mineral medium and 0.1 M NaOH for removing 10% v/v CO_2 in air was used as the preliminary *S. maxima* growth test. Figure 7 shows the change of biomass and pH with cultivation time

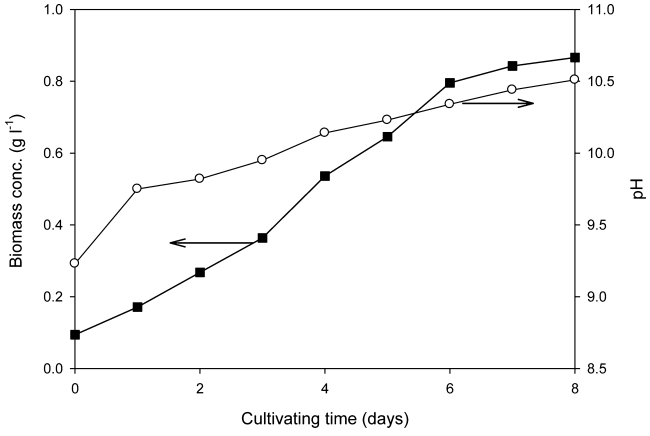

Figure 7. Biomass growth and pH profiles as a function of *S. maxima* cultivation time using the CO_2-enriched RO-water as the growth medium. The RO-water had contained 0.1 M NaOH and been used for absorbing 10% v/v CO_2 in air.

over a cultivation period of eight days. In this experiment, the average biomass productivity was nearly 0.12 g L^{-1} d^{-1} over the initial six days of cultivation. The TIC concentration at the commencement of the cultivation test was about 2140 mg L^{-1}, which was significantly greater than that in the controlled growth tests. This high TIC value apparently led to greater biomass productivity. The biomass growth slowed down after six days partly due to the self-shading effect as the biomass became too dense for effective light penetration (the remaining fraction of light intensity was <1% through the reactor), even the solution was constantly stir-mixed. Meanwhile, the pH of the cultivating solution gradually increased from 9.2 to 10.5 during this period. As opposed to the observed pH decline due to the formation of HCO_3^- (and CO_3^{2-}) during CO_2 absorption by NaOH solutions, the uptake of HCO_3^- for the photosynthetic growth of *S. maxima* caused an increase in pH.

For applying the CO_2-enriched dilute wastewater to cultivate *S. maxima*, the temporal nutrient uptake profiles, including COD, NH_4^+, NO_3^-, PO_4^-, as well as solution pH were shown in Figure 8. With a scrubbing duration of 30 min and a NaOH concentration of 0.5 M, the TIC accumulated in the dilute wastewater for the ensuing cultivation was nearly 1900 mg L^{-1}, resulting in linear biomass productivity of 0.036 g L^{-1} d^{-1}. The pH of the wastewater again rose from 9.2 to 10.3 after eight days, which was consistent with the previous results using CO_2-enriched RO-water. Additionally, the COD reduced from a mean concentration of 275 mg L^{-1} to about 60 mg L^{-1}, corresponding to a removal efficiency of nearly 80%. The BOD (not shown) during the same period was removed from 122 mg L^{-1} to about 42 mg L^{-1}, resulting in a removal efficiency similar to that of COD.

For the nitrogen consumption in the wastewater medium, the mean concentration of NH_4^+ was about halved, whereas that of NO_3^- was unaffected. This result is consistent with the aforementioned growth characteristics of *S. maxima*. Also, PO_4^- was reduced with a limited extent (about 35%). One must note that concentration of NH_4^+, NO_3^-, and PO_4^- (19 mg L^{-1}, 12 mg L^{-1}, 102 mg L^{-1}, respectively) were all markedly lower than

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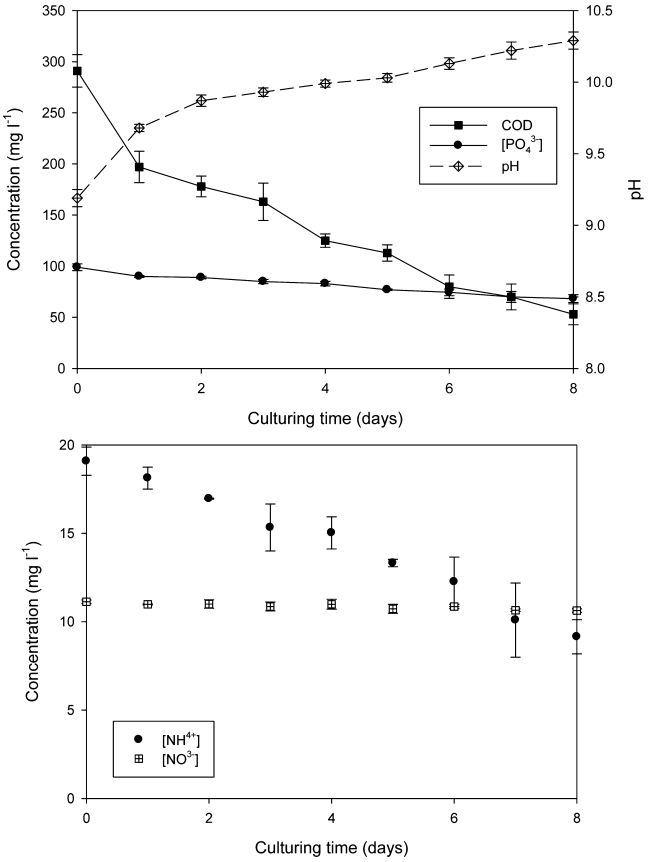

Figure 8. Nutrients uptake from the CO_2-enriched dilute wastewater used for *S. maxima* cultivation. The wastewater had contained 0.5 M NaOH and been used for absorbing 10% v/v CO_2 in air. The error bars represent the standard deviations for the mean values (symbols) of triplicate samples.

those used in the mineral medium (600 mg L^{-1}, 1850 mg L^{-1}, 500 mg L^{-1}, respectively) for the growth tests. In fact, based on the similar accumulated TIC concentrations in presented tests, the low concentrations of nitrogen could be the limiting factor for the biomass growth, as revealed by the significantly greater biomass productivity obtained in the CO_2-enrich RO-water as compared with that in the CO_2-enrich dilute wastewater.

When the 30%-diluted wastewater (dosed with 0.5 M NaOH but no additional nitrogen source) was used for absorbing CO_2 (10% v/v) and subsequently for *S. maxima* cultivation, the biomass yield was limited due the nitrogen deficit. Under such nitrogen limiting condition, the metabolic activities may have persisted, but the photoassimilated carbon is redirected toward the synthesis of carbohydrates until saturation 35. The inorganic carbon conversion ratio to biomass after eight days was only 8.6%, whereas the COD reduction was about 80%. However, when the diluted wastewater was augmented with 0.6 g L^{-1} NH_4NO_3, the inorganic conversion ratio improved to 34%, whereas COD was near completely consumed within six days. As a comparison, when RO water (with negligible COD) was used instead of the diluted wastewater, the carbon conversion ratio was only 22.1%. These results imply that the presence of COD, though without further knowledge of its chemical composition, augmented the biomass growth and carbon conversion. The mixotrophic growth of *Spirulina* has been well documented in the literature, with glucose and acetate as the most common organic carbon sources that enhance the biomass yield.[42−44] It is therefore conceivable that the organic components (e.g., lactose, fats, proteins, and possibly other additives) typically contained in dairy processing wastewater could support cell growth of *Spirulina*. Additionally, studies have also demonstrated that the organic carbon content could support the cell growth for the latter period of a growth cycle when the photosynthetic activity is limited for the light-restricted cultures. Conversely, mixotrophically grown cells showed lower photosynthetic activity, perhaps because the contents of pigments (e.g., chlorophyll-a, carotenoids, and phycocyanin) in these cells were lower than in the autotrophic cultures.[45] In mixotrophic growth, it is also possible that the CO_2 produced from organic carbon metabolism could be used photosynthetically along with HCO_3^- from the culture medium.[46]

This study has demonstrated the feasibility of applying these types of wastewater for CO_2 capturing and microalgae cultivation, which provides dual environmental benefits in the direction of reducing carbon emissions into the atmosphere and wastewater treatment along with sustainable biomass production. However, a certain extent of pretreatment may be needed because the COD concentration in a typical dairy wastewater generally exceeds the tolerable level for photosynthetic growth. In practice, diary wastewater is typically treated by anaerobic digestion processes[47,48] due to its high COD content and potential bioenergy value, or by physicochemical processes such as a combination of de-emulsification, coagulation, flocculation, and dissolved air flotation (DAF). In one possible scenario, the dairy wastewater undergone primary treatment (e.g., de-emulsification, coagulation, and flocculation) removes solids and a fraction of the COD, whereas the nitrogen and phosphorus nutrients are poorly removed.[49,50] Consequently, the pretreated wastewater becomes more viable for the application as proposed in this study.

CONCLUSIONS

This study demonstrated the technical feasibility to use diluted dairy wastewater augmented with NaOH as the liquid sorbent for CO_2 removal from ambient or exhaust air and to use the CO_2-enriched wastewater to support the growth of *S. maxima* without addition of any carbon source. When applying the alkaline wastewater as the scrubbing liquid for removing CO_2 from exhaust such as natural gas boilers, the quantity of CO_2 absorbed and converted into sufficient carbon source to yield substantial biomass productivity that is commercially competitive. In the mean time, the organic pollutants (COD, BOD) and nutrients (NH_4^+, PO_4^-) in the wastewater were partially removed. The treated wastewater, after biomass separation and harvesting, can then be reused as the diluents for the raw wastewater subjected to further carbon scrubbing and microalgae cultivation. The study also showed that the TIC concentration was proportional to the amount of CO_2 absorbed in the scrubbing liquid, and that the solution pH could be used as the controlling parameter in both wet scrubbing stage and biomass cultivation stage in the photobioreactor. These features provide the possible means for online monitoring when the two-stage process operates in commercial scales.

ASSOCIATED CONTENT

Supporting Information

Growth characteristics of *Spirulina* and Adsorption rate and cpapacity of CO_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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