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Short Communication

Estimation of carbon dioxide sequestration potential of microalgae grown in a batch photobioreactor

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HIGHLIGHTS

- High algal growth rate observed with continuous flow of 10% CO_2 enriched air.
- Moles of CO_2 sequestered was determined by mass balance and graphical integration.
- Both strains exhibited maximum carbon sequestration at gas flow rate of 40 ml/min.
- Good correlation observed between moles of CO_2 sequestered and algal growth rate.
- *Chlorella pyrenoidosa* sequestered CO_2 more effectively than *Scenedesmus abundans*.

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ABSTRACT

The carbon dioxide (CO_2) sequestration potential of two microalgae, *Chlorella pyrenoidosa* and *Scenedesmus abundans* was evaluated in a tubular batch photobioreactor with provision for continuous flow of 10% CO_2 enriched air through the headspace. CO_2 sequestration and biomass growth was affected by gas flow rate over the range 20–60 ml/min and 40 ml/min was found to maximize algal growth and CO_2 sequestration. Moles of CO_2 sequestered over 20 h at a gas flow rate of 40 ml/min was estimated using a novel rapid screening approach as 0.096 and 0.036, respectively, for *C. pyrenoidosa* and *S. abundans*. At this gas flow rate the maximum growth rate was 4.9 mg L^{-1} h^{-1} and 2.5 mg L^{-1} h^{-1} for *C. pyrenoidosa* and *S. abundans*, respectively. The CO_2 sequestration and growth rate were comparable at height/diameter ratio of 8 and 16.

1. Introduction

Reducing anthropogenic carbon dioxide (CO_2) emissions is imperative for preventing global warming. The potential of microalgae for capturing CO_2 from simulated flue gases has been demonstrated with CO_2 fixation efficiency in the range of 28–53% (deMorais and Costa, 2007; Goswami et al., 2012; Sydney et al., 2010). The fast growth rate of microalgae can lead to much higher carbon sequestration rates compared to terrestrial plants (Fulke et al., 2010). Carbon sequestration can be maximized through proper choice of species and by optimizing the nutrient availability, light intensity, temperature and pH (Cheng et al., 2013; Jacob-Lopes et al., 2008; Molina Grima et al., 1999). Good carbon sequestration potential of *Chlorella* and *Scenedesmus* species have been widely reported (Fulke et al., 2010; Ho et al., 2010; Tang et al., 2011; Toledo-Cervantes et al., 2013). Proper design and operation of photobioreactors providing sufficiently high surface area to volume ratio (i.e., height (H) to diameter (D) ratio), countercurrent flow of gas and liquid at optimal flow rates and influent CO_2 concentration less than 10% can facilitate the mass transfer of CO_2 and enhance biomass productivity (Molina Grima et al., 1999).

Most researchers have quantified carbon fixation in terms of biomass productivity and CO_2 removal efficiency. There are only limited reports on mass of CO_2 sequestered, its incorporation into algal biomass and variation of these parameters with hydrodynamic conditions (Chiu et al., 2008). The objective of this work was to quantify the CO_2 fixation efficiency of two microalgal strains in a tubular batch photobioreactor with provision for continuous flow of 10% CO_2 enriched air by mass balance on CO_2 and biomass estimation. The optimal conditions for carbon sequestration identified through this approach can provide insights on design of flow through systems and facilitate comparison amongst

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microalgal strains. A novel graphical integration technique was developed to quantify the moles of CO_2 sequestered over a period.

2. Methods

All the chemicals used for preparation of algal growth media were obtained from Merck, India. The chemicals were of analytical grade and had high purity (>99%). *Chlorella pyrenoidosa* (NCIM 2738) and *Scenedesmus abundans* (NCIM 2897) used in this study were obtained from National Collection of Industrial Microorganisms (NCIM), NCL Pune. *C. pyrenoidosa* was subcultured in Fog's medium supplemented with 0.2% KNO_3, whereas *S. abundans* was subcultured in Fog's medium.

2.1. Studies in tubular batch photobioreactor with continuous gas flow

A continuous supply of 10% CO_2 enriched air was provided to three completely mixed tubular batch reactors (CMTBRs) (dimension 18 in. (L) × 1 in. (OD); 220 ml total volume and 100 ml aqueous phase volume) connected in parallel. The gas was delivered at the base of the tubular reactor through a silica diffuser such that the bubbles traversed up through the water column before exiting the reactor. Illumination was provided using a fluorescent lamp (85 W) aided with a mirror arrangement such that the CMTBRs were exposed to 8000 lux (Fig. S1, Supplementary material). One CMTBR served as the un-inoculated control. The other two CMTBRs were inoculated with the desired strain of microalgae grown up to end of log phase and the experiments were conducted over a duration of 20–30 h. Studies were conducted using *C. pyrenoidosa* and *S. abundans*. Constant flow rate of 10% CO_2 enriched air was maintained using a rotameter. Periodic gas sampling was conducted at the gas influent and effluent ports using water filled glass sampling bottles in which the gas was allowed to partially displace the water before the valves were closed. Biomass concentration at any time was determined as volatile suspended solids (VSS).

Initially a study was conducted to determine the impact of carbonate (CO_3^{2-}) in the media on CO_2 sequestration by *C. pyrenoidosa*. One of the CMTBRs was used as un-inoculated control whereas the others were inoculated with *C. pyrenoidosa* (initial VSS = 9.2 mg L^{-1}). Of the two inoculated CMTBRs, one contained Fog's media with carbonate (5 mg L^{-1} Na_2CO_3) while the other contained media devoid of carbonate. 10% CO_2 enriched gas was bubbled at 40 ml min^{-1} flow rate. Subsequently, studies were conducted to determine the effect of flow rate (20, 30, 40, 60 ml min^{-1}) on CO_2 sequestration for both *C. pyrenoidosa* and *S. abundans* in media devoid of carbonate. The impact of H/D ratio variation was studied by doubling the working volume of the reactor. This study was conducted in presence of *C. pyrenoidosa* and a gas flow rate of 20 ml min^{-1} was used. All studies were conducted in duplicate and the error bars depict standard error (SE). Algal growth rate and SE in growth rate for studies in the photobioreactor was obtained based on linear regression of VSS data collected over the first 16 h. All statistical analysis was performed using Statistica, version 8.

2.2. Analysis of CO_2 in gas phase

The gas samples were analyzed using a gas chromatograph equipped with a thermal conductivity detector (Nucon, 5765, India) and a stainless steel packed column with carbosphere packing (6″ (L) × 0.125″ (OD)) was used as per the method reported by Hwang et al. (2001). Argon was used as carrier gas at a flow rate of 40 ml/min. The sample (0.5 ml) was injected with a gas tight syringe. A gas standard mix (Master speciality gases Pvt. limited) was used for calibration. It contained a mixture of hydrogen, nitrogen, carbon monoxide, methane and CO_2 at mole % of 19%, 25%, 25.2%, 5.5% and 25.3%, respectively. Retention time of CO_2 was 6.86 min. Partial pressure of CO_2 (or mole fraction of CO_2) in any gas sample was quantified against the external standard.

2.3. Estimation of CO_2 sequestration over 20 h

The moles of CO_2 sequestered in algal biomass after a fixed time was determined as follows:

$$M = \int_{t_0}^{t} (F_{\text{in}} - F_{\text{out}})dt \tag{1}$$

$$F = Q_g\ C_g \tag{2}$$

$$C_g = P_i/(RT) = p_i P_T/(RT) \tag{3}$$

where, F = molar flow rate of CO_2 (mole h^{-1}); Q_g is the volumetric flow rate (L h^{-1}) and C_g is the gas phase concentration of CO_2 (mole L^{-1}), P_i is the pressure exerted by CO_2, p_i is the partial pressure of CO_2, P_T is total pressure, R is the universal gas constant and T is absolute temperature (K). The mole fraction CO_2 in the gas phase is same as the partial pressure of CO_2. Partial pressure of CO_2 in the inlet ($p_{i,\text{in}}$) and outlet gas ($p_{i,\text{out}}$) was used to compute molar flow rate of CO_2 (F, mole h^{-1}). The $p_{i,\text{in}}$ was held constant (=0.1).

3. Results and discussion

3.1. Effect of addition of carbonate to the nutrient medium

CO_2 in the outlet gas from the CMTBRs was monitored for *C. pyrenoidosa* grown in presence and absence of carbonate over a period of 20 h. Negligible removal of CO_2 from the gas phase was observed in the controls devoid of algae such that CO_2 mole fraction in the outlet gas remained essentially constant and equal to that in the inlet. For the CMTBRs with algae, CO_2 removal from the gas phase was observed since algal utilization of CO_2 continuously lowered the concentration of inorganic carbon in the liquid phase compared to that based on equilibrium considerations. Thus, CO_2 from the gas stream was dissolved forming carbonic acid ($H_2CO_3^*$) which was instantaneously dissociated into bicarbonate and carbonate ions (HCO_3^- and CO_3^{2-}) depending on the pH of the system. Increasing the liquid phase inorganic carbon concentration using Na_2CO_3 was found to lower the removal of CO_2 from the gas phase. *C. pyrenoidosa* grown in medium with no externally added carbonate showed greater utilization of CO_2 (Fig. S2). After 20 h, CO_2 mole fraction in the outlet was 0.038 and 0.008 for *C. pyrenoidosa* grown in presence and absence of carbonate, respectively. Throughout, the rate of CO_2 sequestration was significantly lower when carbonate was present in the medium. This is in agreement with literature reported observations. Carbon provided as gaseous CO_2 versus dissolved inorganic carbon, i.e., H_2CO_3, HCO_3^- and CO_3^{2-}, is not a critical issue in algal cultivation since these reactions interconvert sufficiently fast and CO_2 utilization by the algal cells is the rate limiting step (Molina Grima et al., 1999). The difference in CO_2 mole fraction in the effluent gas in presence and absence of Na_2CO_3 in the media was statistically significant ($p < 0.05$).

3.2. Effect of flow rate on CO_2 sequestration and algal growth rate

The impact of flow rate on CO_2 sequestration was determined using gas flow rates of 20, 30, 40 and 60 ml min^{-1} in the CMTBRs. Figs. 1 and 2 illustrates the CO_2 mole fraction in the outlet gas and increase in VSS due to growth of *C. pyrenoidosa* and *S. abundans*. The outlet CO_2 profile showed a decrease over the period 4–16 h