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Review

Development of suitable photobioreactors for CO_2 sequestration addressing global warming using green algae and cyanobacteria

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ABSTRACT

CO_2 sequestration by cyanobacteria and green algae are receiving increased attention in alleviating the impact of increasing CO_2 in the atmosphere. They, in addition to CO_2 capture, can produce renewable energy carriers such as carbon free energy hydrogen, bioethanol, biodiesel and other valuable biomolecules. Biological fixation of CO_2 are greatly affected by the characteristics of the microbial strains, their tolerance to temperature and the CO_2 present in the flue gas including SO_X, NO_X. However, there are additional factors like the availability of light, pH, O_2 removal, suitable design of the photobioreactor, culture density and the proper agitation of the reactor that will affect significantly the CO_2 sequestration process. Present paper deals with the photobioreactors of different geometry available for biomass production. It also focuses on the hybrid types of reactors (integrating two reactors) which can be used for overcoming the bottlenecks of a single photobioreactor.

1. Introduction

Global warming has been reached to an alarming level due to the change in global environment. Industries related to electricity generation, natural gas processing, cement, iron and steel manufacturing, combustion of municipal solid waste are the major contributors of atmospheric CO_2 because of their dependence on carbon sources like coal, oil, natural gas for fulfilling their energy requirement (Inventory of U.S greenhouse gas emissions and sinks: 1990–2008). According to the report of carbon dioxide information analysis center (CDIAC), CO_2 emissions have increased from 3 metric tons in 1751 to 8230 metric tons in 2006. Alarming feature of CO_2 emission can be understood by the trends of its presence in atmosphere at Mauna loa observatory (Hawaii, US) which shows 390 ppmv in 2010 compared to 280 ppmv in 1958. Keeling curve clearly indicates initially the slow and latter progressively faster rise in the concentration of CO_2 (Tans, 2010). Sequestrations of CO_2 from the industries are today's demand in order to reduce the impact of CO_2 on global warming. Sequestration strategies adopted so far can be broadly divided into physical and biological means. Physical means of CO_2 sequestration has disadvantages, having high costs associated with it thereby need to develop the suitable technologies. Capturing, transporting and storing CO_2 are also very expensive processes. Biological method of CO_2 sequestration is an alternative to physical methods. The use of algae for CO_2 sequestration has several advantages: mitigating CO_2, the major source of global warming as well as producing biofuels and other interesting secondary metabolites. One kilogram of algal dry cell weight utilizes around 1.83 kg of CO_2. Annually around 54.9–67.7 tonnes of CO_2 can be sequestered from raceway ponds corresponding to annual dry weight biomass production rate of 30–37 tonnes per hectare (Brennan and Owende, 2010). Algal biomass can be used for the production of biofuels (e.g. biodiesel, bioethanol, biohydrogen) and other commercially and scientifically important products like industrial biofilters, food products, water quality testing (Loubiere et al., 2009). The major problem associated with the biological use of CO_2 are the high temperatures of flue gas and the presence of NO_x, SO_x as well as other impurities of the fossil fuel used. For the cultivation of algae for CO_2 sequestration both open as well as closed systems are used. However, open system has disadvantage to control parameters like availability of light, agitation, pH, temperature and nutrient concentrations. Fluctuation in temperature and light availability due to diurnal cycles and seasonal variations are a major problem for open systems (Brennan and Owende, 2010). Use of open system for sole aim of CO_2 sequestration is being downplayed because of the very low residence time of the sparged gas in the culture which gives very little time to algal biomass to sequester CO_2 from flue gas. It is also susceptible for high contamination which reduces the biomass productivity and its use for the production of commercially important products. In a closed system the degree of control is very high and it is possible to control crucial parameters that influence the culture (Carvalho et al., 2006).

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Table 1
Temperature and flue gas tolerance of various algal species (Ono and Cuello, 2004).

Algal species	Maximum temperature tolerance (°C)	Maximum CO_2% (v/v) tolerance	Maximum SO_x (ppm) tolerance	Maximum NO_x (ppm) tolerance	References
Cyanidium caldarium	60	100	–	–	Seckbach et al., 1972
Scenedesmus sp.	30	80	–	–	Hanagata et al., 1992
Chlorococcum littorale	–	70	–	–	Ota et al. 2009
Synechococcus elongates	60	60	–	–	Miyairi. 1995
Euglena gracilis	–	45	–	–	Nakano et al., 1996
Chlorella sp.	45	40	–	–	Hanagata et al., 1992
Chlorella sp. HA–1	–	15	–	100	Yanagi et al., 1995
Eudorina sp.	30	20	–	–	Hanagata et al.,1992
Dunaliella tertiolecta	–	15	–	1000	Nagase et al., 1998
Chlamydomonas sp. MGA 161	35	15	–	–	Miura et al., 1993
Nannochloris sp.	25	15	–	100	Yoshihara et al., 1996
Tetraselmis sp.	–	14	185	125	Matsumoto et al., 1995
Monoraphidium minutum	25	13.6	200	150	Zeiler et al., 1995
Spirulina sp.	–	12	–	–	de Morais and Costa, 2007
Chlorella sp. T-1	35	–	20	60	Maeda et al., 1995

This paper is mainly focused on factors affecting the sequestering of CO_2 from industrial flue gas by microalgae and discussed about the various types of photobioreactors with different geometries and parameters implemented for CO_2 sequestration and biomass production. It also gives a clear view on suitable photobioreactors for CO_2 sequestration to be used in the future.

2. Microbiology

Green algae and cyanobacteria (formally blue-green algae) comprise a vast group of photosynthetic organisms. They are ubiquitously distributed throughout the biosphere and grow under the widest possible variety of conditions from aquatic (freshwater to extreme salinity) to terrestrial places. Its uniqueness that separates them from other microorganisms is due to presence of chlorophyll and having photosynthetic ability in a single algal cell, therefore allowing easy operation for biomass generation and effective genetic and metabolic research in a much shorter time period than conventional plants. Well defined nucleus, a cell wall, chloroplast containing chlorophyll and other pigments, pyrenoid, a dense region containing starch granules on its surface, stigma, and flagella are the major components of green algae (Michael et al., 2008). Filamentous colonies of cyanobacteria have ability to differentiate into different cell types like vegetative cells, akinetes, and heterocysts. General function of vegetative cells, akinetes and heterocysts are ability to carry out complete oxygenic photosynthesis, resistance for climate and having a potential to fix nitrogen, respectively. Heterocysts contain the enzyme complex nitrogenase which converts atmospheric nitrogen into ammonium, a unique capacity among photosynthetic oxygenic organisms. These are the only known prokaryotes having oxygenic photosynthesis for fixation of CO_2 like eukaryotic algae and plants (Michael et al., 2008).

3. Biochemistry of CO_2 fixation

In a multistep process of photosynthesis plants and algae (green algae and cyanobacteria) fix CO_2 into sugar using light and water as energy and electron source, respectively. The overall reaction for photosynthesis is given by:

$$CO_2 + H_2O + \text{light} \rightarrow (CH_2O)_n + O_2$$

The step of photosynthesis in which CO_2 is converted into sugar with the help of ATP (adenosine-5′-triphosphate) by the carboxylase activity of the enzyme ribulose 1,5-bisphosphate carboxylase/oxygenase (RuBisCO), is called as Calvin cycle (Nelson and Cox, 2005). Synthesis of one mole CH_2O, requires a minimum of 8 mol of photons (quanta) each having 218 kJ of energy per mol. Photosynthesis converts approximately 27% of solar energy into chemical energy as it produces 467 kJ of energy per mol of CH_2O as against 1744 kJ required per mol for its formation (Brennan and Owende, 2010). Concentration of CO_2 in water in equilibrium with air is approximately 10 μM. However, since RuBisCO has low affinity for CO_2, at the normal atmospheric level of CO_2 (390 ppmv) it is only half saturated with the CO_2. Moreover it also performs oxygenase activity which produces glycolate 2-phosphate as the end product. It has no use to cell and its synthesis consumes significant amount of cellular energy and also releases previously fixed CO_2 by the carboxylase activity of RuBisCO. The oxygenase activity of RuBisCO inhibits biomass formation of around 50% (Giordano et al. 2005). To overcome the low affinity of RuBisCO for CO_2, most algae and cyanobacteria have different CO_2 concentrating mechanisms (CCMs). CCMs activates only at low dissolved carbon concentration. The maximum value of dissolved inorganic carbon till which it is active depends upon strain, pH, light availability, preadaptation of cells etc. For example, in cyanobacteria $K_m(CO_2)$ is 200 μM as against approximately 10 μM dissolved CO_2 in water in equilibrium with air (Moroney and Somanchi, 1999). Similarly, in *Chlorella ellipsoidea* at pH 7.5, the minimum equilibrium dissolved inorganic carbon (DIC) concentration at which high CO_2 characteristics were maintained, i.e. transport was repressed, was 2100 μM, whereas the maximum equilibrium DIC concentration below which DIC transport was fully induced was 500 μM (Matsuda and Colman, 1995). CCMs acts as an enhancer for higher growth rates in algae and hence can be used for improvement in photobioreactor productivity (Ramanan et al., 2010). The expression of the enzyme carbonic anhydrase (CA) has been associated with

induction of the CCMs. CA catalyzes the interconversion of CO_2 and HCO_3^- and is an important component in the intracellular mobilization of the HCO_3^- pool, by catalyzing the production of CO_2 for RuBisCO (Matsuda and Coleman, 1995).

$$CO_2 + H_2O \rightarrow HCO_3^- + H^-$$

4. Sources of CO_2

Combustion of fossil fuel such as coal, oil, and gas is the largest source of CO_2 emissions globally. Flue gas emitted from these sources mostly contains nitrogen (N_2), CO_2, oxygen (O_2), and water vapour. It also contains minor amounts of CO, NO_x, SO_x and particulate matters. Characteristics of flue gas obtained by authors from Kolaghat thermal power station, India shows that percentage of CO_2 in the flue gas was 11.2% (v/v) while SO_x and NO_x were 672.0, 610.08 mg/Nm^3, respectively. Flue gases data obtained by Berberoglu et al. (2009) from fossil fuel power plants also consisted of 4–14% of CO_2 and up to 200 ppm of NOx and SO_x depending on the type of fuel and its type of combustion process. Coal fired plants generally have higher percentage of CO_2 emissions (Packer, 2009). Power plants can use electrostatic precipitator for removing dust particles. Some of them also have desulfurization and denitrification facility for the removal of oxides of sulphur and nitrogen, respectively (Maeda et al., 1995). The composition of the flue gas of coal fired thermal power plants after passing through electrostatic precipitator and desulfurization facility was 13% CO_2, 5% O_2, 10 ppm or below SO_x, 150 ppm or below NO_x, and 10 mg/Nm^3 or below dust (Maeda et al., 1995). NO_x present in the flue gas generally poses no problem for algal growth while the main impact is due to SO_x which decreases the pH due to formation of sulphurous acids (Packer, 2009). Finally the choice of CO_2 point source depends on the cost associated with it which varies from point source to point source. It is approximately $6–$12, $5–$70, $20–$95 , $30–$145 per ton CO_2 from ethanol facilities, hydrogen and ammonia production or gas-processing plants , fossil power plants and other industrial sources, respectively (Xu et al., 2010).

5. Factors affecting the CO_2 sequestration process

5.1. Temperature

Temperature of flue gas emitted from power plants and other sources are around 120 °C. Feasibility of sequestering CO_2 from flue gas depends on either installing heat exchanger system or using thermophilic species. Several species have been identified which can tolerate high temperature up to 60 °C (Table 1). When the unicellular cyanobacterium *Synechococcus elongates* was bubbled with various concentration of CO_2 at different temperature, it was found that a drop in pH at 52 °C with 60% CO_2 was comparable to a drop in pH at 25 °C with 20% CO_2 suggesting that the temperature dependent solubility of CO_2 gives an advantage to thermophilic algae to tolerate a higher concentration of CO_2 (Miyairi, 1995). Ratio of O_2 to CO_2 solubility increases with the temperature causing significant amount of O_2 fixation by oxygenase activity of RuBisCO. In addition RuBisCO affinity for CO_2 also decreases on increasing temperature.

5.2. pH

The pH of the culture medium can be influenced by dissolving CO_2 and SO_x from the flue gas. With elevated CO_2 concentrations, pH drops down to pH 5, and with higher SO_x concentrations even down to pH 2.6 have been reported (Maeda et al., 1995; Westerhoff et al., 2010). Whereas the pH change due to the CO_2 had just minor influence on the algal growth, the strong pH change caused by the SO_x inhibited all growth. With buffered medium the pH drop could be prevented and almost no changes in growth rates compared to lower SO_x concentrations were observed (Maeda et al., 1995). This indicates that the influence of SO_x on the growth is, in certain limits mainly due to pH changes than sulphate concentrations in the medium, which can be prevented by buffering or active pH control.

5.3. NO_x and SO_x in the flue gas

Besides high amount of CO_2 and high temperature, NO_x and SO_x influence the growth of the microalgae. Tolerance of microalgae to NO_x and SO_x varies widely among the various species (Table 1). *Nannchloris* can grow below 100 ppm of NO_x (Yoshihara et al., 1996) on the other hand species like *Dunaliella tertiolecta* can grow in up to 1000 ppm of NO_x (Nagase et al., 1998). *Tetraselmis* sp. can grow in the combination of 125 ppm NO_x and 185 ppm SO_x (Matsumoto et al., 1995). Experiment conducted by Maeda et al. (1995) on *Chlorella* sp.T-1 confirms the tolerance of this species under 20 ppm SO_x and 60 ppm NO_x. *Chlorella* sp. HA-1 was found to have a higher tolerance capacity than *Chlorella* sp. T-1 as it can tolerate up to 100 ppm of NO_x along with 10–15% CO_2. However, *Chlorella* sp. HA-1 could not grow under higher combination of SO_x and NO_x because of a drastic decrease in pH (Yanagi et al., 1995). Adding certain amounts of sodium sulphite instead of gaseous SO_2 to the medium resulted in a slower growth at 50 mM and cell death at 250 and 500 mM (Maeda et al., 1995).

5.4. Light

For the CO_2 fixation and biomass production optimum light intensity is necessary. Below the optimum light intensity, light becomes the limiting factor for the microalgal productivity. While exposure of cells to long period with high light intensity causes photoinhibition due to damage of repair mechanism of photosystem II leading to inactivation of other systems including the oxygen evolving systems, electron carriers and the associated D1/D2 proteins (Rubio et al., 2003). Light intensity at the depth of dense algal suspension is greatly reduced because of the absorption and scattering of light. Attenuation of light intensity is dependent of its wavelength, cell concentration, penetration distance of light and the geometry of photobioreactor. Since the blue and red light are mostly consumed by the microalgae, it penetrates little in microalgae suspension than green light. This effect is more pronounced in the dense culture. In the engineering point of view geometry of reactor can reduce the attenuation of light in micro algal suspension. Fernandes et al. (2010) studied the effect of circular and plan geometry in light penetration. For similar microalgae cell concentrations, circular geometry allows a better light penetration, than the plane geometry allowing a higher volume fraction of the reactor to receive sufficient amounts of light however, plan geometry helps in uniform distribution of light (Fernandes et al., 2010). Saturation light intensity (I_s) is one of the important parameter which determines the light utilization efficiency and overall photosynthetic efficiency. Pigments present within the photo system are overloaded with the incoming light and interrupt the alteration of light harvesting complex synthesis and degradation. This results in the production of reactive oxygen species causing photoinhibition and/or photo oxidative death (Torzillo et al., 2003). Saturation light intensity roughly varies from 30 to 45 W/m^2 (140–210 μE m^{-2} s^{-1}) with a good estimation. For example, according to Hanagata et al. (1992) saturation light intensity of *Chlorella sp.* and *Scendesmus sp.* is around 200 μE m^{-2} s^{-1}. In outdoor condition, light availability is the dominant factor determining the productivity. Light saturation imposes serious problem for the growth of algae at the

central daylight hours where solar irradiance can exceed 2000 μmol photons m^{-2} s^{-1}(Cuaresma et al., 2009). Light utilization efficiency (E_s) and overall photosynthetic efficiency (E_r) are greatly dependent on the ratio of incident light intensity (I_o) and saturation light intensity (I_s) (Torzillo et al., 2003). Mathematically it can be described by.

$$E_s = \frac{l_s}{l_0}(ln\frac{l_0}{l_s} + 1)$$

Above equation is valid only for $I_o/I_s > 1$. For $I_o/I_s \leqslant 1$, E_s and E_r are 1 and 0.2, respectively. It is clear that E_s and E_r are significant only when ($I_o/I_s < 10$). It is worth to note that productivity does not necessarily dependent on light utilization efficiency. Above equation successfully explains the light utilization efficiency but productivity does not maintain a constant maximum value when all the values of (I_o/I_s) are less than one. It increases from its minimum value and after increasing proportionally with the light conversion efficiency becomes constant on achieving 100% light utilization efficiency. (I_o/I_s) effect needs to be considered for efficient CO_2 sequestration and biomass productivity. For better utilization of light photo bioreactor should be designed in such a way to minimize (I_o/I_s) which can be done by either decreasing I_o and/or increasing I_s. Therefore selection of algal species having high I_s is advisable. Following approaches have been proposed for decreasing I_o.

5.4.1. Proper mixing

Proper mixing not only helps in the uniform mixing of nutrient but also in the better distribution of light over cells. It minimizes the I_o and also takes advantage of flashing light effect. This effect increases the productivity in tubular photo-bioreactor up to 40% (Ugwu et al., 2002). Ultra high density of *Spirulina* is tried to reduce I_o and photoinhibition effect in flat photobioreactor by Hu et al. (1996). Carlozzi and Torzillo (1996) also tried to take advantage of mixing by constructing strongly curved tubular photobioreactor allowing cells exposed to higher light at the surface to go inner region reactor and hence limiting cells from taking higher value of I_o.

5.4.2. Photobioreactor design

The light distributes efficiently in the whole region of culture in photobioreactor having larger optical cross sectional area. Many photobioreactors have been tried having special designed light system to distribute the intense light for taking advantage of diluted light for the efficient CO_2 sequestration and biomass formation (Lee et al., 1995; Morita et al., 2000). Suh and Lee (2003) have designed internally illuminated airlift photo-bioreactor to study the light distribution for maximizing the growth efficiency of photosynthetic cells using *Synechococcus sp.* PCC 6301. Zijffers et al. (2008) constructed a flat plate photobioreactor in which the sunlight is focused on the top of the bioreactor by dual-axis positioning of linear Fresnel lenses, captured by vertical plastic light guides, reflected internally in these guides, and then eventually distributed into the photobioreactor compartment. With this design, the sunlight can be more evenly distributed in the bioreactor and better light utilization is expected.

5.4.3. Biological pigment reduction

Uniform and impartial distribution of incident light (I_o) to every layer of cells can be achieved by using the algal strains having small antenna size. In normal case first layer of cells gets maximum light and decreases drastically to the consecutive further layers of cells. A small antenna size strain reduces this wastage of light and prevents the cells from photoinhibition and dissipation of light through non-photochemical quenching (Torzillo et al., 2003). This would in turn allow researchers to use high density cells and increasing the optical path length resulting in higher photosynthesis rate and its productivity (Nakajima et al., 2000). Reducing the chlorophyll concentration is another such method. Basic science behind this idea is that by limiting the cells from excess chlorophyll concentration, higher cell density can be used which in turn results in higher productivity. A patent is filed by Kizililsoley et al. (2008) claiming 10 times higher aerial productivity in open ponds using *Spirulina* as a model microorganism. This strategy can also be used in achieving higher aerial CO_2 sequestration, biomass formation and e.g. hydrogen production in photo-bioreactors.

5.5. Culture strain

Selection of culture strains are the foremost important aspect to take care for the mitigation of CO_2. High growth rates, temperature range, resistivity to shear stress are the important criteria in deciding the suitability of strain for CO_2 sequestration. In terms of cell fragility *Dunaliella* represents an extremely fragile species because of lack of cell walls while other algal species like *Spirulina* can tolerate relatively higher level of stress. Sensitivity of secondary metabolite like carotenoid astaxanthin producer *Haematococcus* varies with respect to its cell cycle. Resistance to shear stress increases greatly from green to red phase. Its sensitivity in green phase is because of the deflagellation while its resistance in red phase is due to presence of immobile aplanospores. Yoo et al. (2010) has reported that *Scenedesmus* sp. is more appropriate to mitigate CO_2 due to its high biomass productivity and C-fixation ability. Efficiency of CO_2 removal or fixation depends on physiological conditions of microalgae like potentiality for cell growth and their ability of CO_2 metabolism (Yoo et al., 2010). Strains suitable for CO_2 sequestration should have low risk of contamination and should produce high value products (Lopez et al., 2009). Recently, Westerhoff et al. (2010) reported about microalgae tolerant to high levels of carbon dioxide. They isolated *Scenedesmus* and *Chlorella* species from a limestone mineral hot spring with elevated dissolved CO_2 levels, which grew at CO_2 concentrations in the gas phase of up to 40% without significantly changed growth rates. Maximum CO_2 tolerance capabilities of different algal species are tabulated in Table 1.

5.6. Culture density

Productivity and light utilization efficiency value are the functions of the cell density. It is crucial to select the optimum cell concentration for the efficient CO_2 sequestration. Below the optimum cell concentration, not all the light energy is captured by the cells while at above the optimum cell concentration, a larger proportion of the cell are in the dark due to self-shading (Zhang et al., 2001). When *Synechocystis aquatilis* SI-2 was cultivated in flat panel reactor in outdoor condition at 40 °C with various level of irradiation, a cell concentration in the range of 1–2 g L^{-1} is found to be the optimum. Bell shaped relationship between biomass productivity and cell concentration have been reported in flat inclined modular and vertical flat plate photobioreactor by Hu et al. (1996) and Zhang et al. (2001), respectively. However, highly dense culture also makes cells more tolerant to high percentage of CO_2 concentration (Chiu et al., 2008).

5.7. CO_2 concentration

In aquous environment dissolved CO_2 always exist in euilibrium with H_2CO_3, HCO_3^- and CO_3^{2-} which concentration depends upon pH and temperature. Due to fast interconvertible reacton among them, consumption of any of inorcanic carbon does not affect the equilibrium. Microalgal cells preferentially uptake HCO_3^- over CO_2 despite of the fact that former is a poor source of carbon than later (Carvalho et al., 2006).

Table 2
CO_2 sequestration capabilities of different algal species.

Algal species	% CO_2 at influent (% v/v)	Flow rate (vvm)	% CO_2 sequestered	Mode of operation	Type of photobioreactor	Amount of CO_2 sequestered (g h^{-1})	Maximum biomass produced (g L^{-1})	Biomass productivity (mg dwt L^{-1} d^{-1})	CO_2 fixation rate	References
Chlorella sp.	Air	–	–	–	Bubble column	–	0.682 ± 0.007	–	–	Chiu et al., 2008
	2	–	58	–		0.261	1.445 ± 0.015	–	–	
	5	–	27	–		0.316	0.899 ± 0.003	–	–	
	10	–	20	–		0.466	0.106 ± 0.001	–	–	
	15	–	16	–		0.573	0.099 ± 0.001	–	–	
Chlorella vulgaris	10	–	–	–	–	–	–	104.76 ± 10.73	–	Yoo et al., 2010
Scenedesmus obliquus	10	–	–	–	–	–	3.13	217.50 ± 11.24	–	Do
	5.5 (flue gas)	–	24		–	–	–	203	–	
Botrycoccus braunii	10	–	–	–	–	–	–	26.55 ± 7.66	–	Do
	5.5 (flue gas)	–	–	–	–	–	–	77	–	
Spirulina sp.	6	–	53.29	–	Three– stage serial tubular	–		220	–	de Morais and costa, 2007
	12	–	45.61	–		–	3.5	–	–	
Synechocystis aquatilis SI-2	10	0.05	–	Continuous	Vertical flat-plate	–	–	30 g m^{-2} day^{-1}	50 g m^{-2} day^{-1}	Zhang et al. 2001
Anabaena sp. ATCC 33047	Air	0.2	–	Continuous	Bubble column	–	–	0.31 g L^{-1} day^{-1}	1.45 g L^{-1} day^{-1}	Lopez et al. (2009)
Phaeodactylum tricornutum	60	–	63	–	Airlift	–	6.2	–	2.47 g L^{-1} day^{-1}	Sobczuk et al., 2000

Table 3
Performance of different photobioreactors.

Microalgal species	Mode of operation	Types of photobioreactor	Volume of the reactor (L)	Maximum biomass produced (g L^{-1})	Biomass productivity (g L^{-1} d^{-1})	References
Phaeodactylum tricornutum	Continuous	Tubular	200	–	1.9	Molina et al., 2001
Phaeodactylum tricornutum	Continuous	External loop airlift tubular	200	–	1.2	Fernandez et al., 2001
Phaeodactylum tricornutum	Continuous	Helical tubular	75	–	1.4	Hall et al., 2003
Dunaliella tertiolecta	Continuous	Flat panel	3.4	2.46	–	Barbosa et al., 2005
Nanochloropsis	Continuous	Flat panel	440	–	0.27	Cheng-Wu et al., 2001
Haematococcus pluvialis	Continuous	Tubular	25,000	–	0.052	Olaizola., 2000
Spirulina platensis SP-G	Semicontinuous	Helical tubular	21	–	0.4	Travieso et al., 2001
Arthrospira platensis M2	–	Coiled tubular	120	–	0.9	Tredici and Zittelli, 1998
Arthrospira platensis M2	–	Flat chamber	7	–	1.93	Do
Arthrospira platensis M2	–	Curved chamber	7	–	1.64	Do
Arthrospira platensis M2	–	Near horizontal tubular	34	–	1.26	Do
Arthrospira platensis M2	–	Near horizontal flat panel	34	–	1.09	Do
Chlorella sorokiniana	Continuous	Flat panel	1.6	–	12.2	Cuaresma et al., 2009
Haematococcus pluvialis	Continuous	Airlift reactor	50	–	0.7	Garcia-Malea et al., 2009

Algal cells can tolerate CO_2 only up to a certain level after which it becomes detrimental for the growth of the cells because of the two reasons. Firstly environmental stress induced by the higher CO_2 concentration which causes biological reduction in the capacity of algal cells for CO_2 sequestration (Sobczuk et al., 2000). Secondly at higher CO_2 concentration, the culture pH decreases due to the formation of high amount of bicarbonate buffer (which is described elsewhere). The biomass productivity increases with increase in CO_2% (v/v) in the gas mixture up to certain percentage beyond which productivity decreases (Table 2). CO_2 sequestration experiment conducted by Chiu et al. (2008) at a flow rate of 0.25 vvm reports that 2% (v/v) of CO_2 is optimum for the growth of *Chlorella* while at 10% (v/v) specific growth rate becomes insignificant. However, the experiment conducted by Maeda et al.

(1995) for the sequestration of CO_2 from flue gas emitted by coal fired thermal power plant confirms that *Chlorella* sp. T-1 can tolerate up to 100% CO_2 concentration but the maximum growth rate was obtained when using 10% CO_2 with no significant decrease in growth rate up to 50% CO_2 concentration. They also concluded that preadaptation of cells with lower percentage of CO_2 concentration leads the tolerability of cells in higher percentage of CO_2.

5.8. CO_2 mass transfer

Volumetric mass transfer coefficient (K_La) is the characteristics of the bioreactor and determines the capability of reactor to sustain optimum cell growth. Behaviour of K_La and cell growth rate varies in the different region of liquid flow. Liquid flow region in photobioreactor can be divided into bubble flow, transition and heterogeneous zone depending upon gas velocity. In the bubble flow region, gas hold-up, interfacial area and K_La is proportional to the gas superficial velocity. Although decrease in interfacial area start on moving from transition zone to heterogeneous zone but gas hold up and K_La achieves plateau. Corresponding to increase in K_La, initially specific growth rate increases but from the end of the transition zone, it starts decreasing. Shear stress may be possible reason for the fall in specific growth rate (Contreras et al., 1998). Zhang et al. (2002) did the comparative analysis of K_La in different photobioreactor in different percent of CO_2 and concluded that requirement of critical K_La increases with decrease in the concentration of CO_2 in the inlet gas stream to meet the CO_2 demand of microalgal cells (Zhang et al., 2002).

5.9. O_2 accumulation

The water splitting activity of photosystem II is responsible for the oxygen evolution during photosynthesis. Trapped oxygen in the liquid culture causes toxic effects like photo-bleaching and reduces the photosynthetic efficiency. An efficient degassing system is required in order to remove formed O_2. Accumulation of O_2 is a serious problem in reactors with poor gas exchange like horizontal tubular reactors, especially when continuous run tubing increases (Miron et al., 1999). The problem of accumulation of O_2 increases when a helical tubular reactor is scaled-up by increasing the light harvesting unit. Hence it is necessary to have a separate degassing unit in which the distance between the entrance and exit is such that even smallest bubbles can disengage. It is not of major concern in reactors which have an open gas transfer area as in stirred tank and vertical reactors.

6. Different photobioreactors configurations and their advantages and disadvantages

Bioreactors suitable for CO_2 sequestration have flexibility of using CO_2 rich gas as a means of mixing as well as providing nutrient for the growth of algae. Generally in this type of reactor, agitation is done non-mechanically like airlift, bubble column, tubular reactor, flat panel etc. There are also few bioreactors where agitation can be done by mechanical means as well as by bubbling through CO_2 rich inlet gas like stirred tank. High mass transfer is the requisite criteria for the bioreactors designed especially for CO_2 sequestration. CO_2 from the gaseous phase transfers inside the algal cells through liquid phase and so increases the resistance to mass transfer. Different types of bioreactors for CO_2 sequestration are in operation at Indian Institute of Technology Kharagpur, India. Based on the geometric features of different photobioreactors, their performance in CO_2 sequestration process varies. Few commercially available photobioreactors are tabulated in Table 3. Bioreactors can be categorized in the following terms.

6.1. Vertical tubular photobioreactor

It is made up of vertical tubing that is transparent in nature to allow the penetration of light. Sparger is attached at the bottom of the reactor which converts the sparged gas into tiny bubbles. Sparging with gas mixture provides overall mixing, mass transfer of CO_2 and also removes O_2 produced during photosynthesis. Vertical tubular photobioreactors can be divided into bubble column and airlift reactor based on their mode of liquid flow.

6.1.1. Bubble column photobioreactor

Bubble column reactors are cylindrical vessel with height greater than twice the diameter. It has advantage of low capital cost, high surface area to volume ratio, lack of moving parts, satisfactory heat and mass transfer, efficient release of O_2 and residual gas mixture. Mixing and CO_2 mass transfer is done through bubbling the gas mixture from sparger. In scale-up, perforated plates are used in tall bubble column to break up and redistribute coalesced bubbles (Doran, 1995). Light is provided externally. Photosynthetic efficiency greatly depends on gas flow rate which depends on the light and dark cycle as the liquid circulated regularly from central dark zone to external photic zone at higher gas flow rate. At gas flow rate less than $\leqslant 0.01\ m\ s^{-1}$ circulation flow pattern does not exist because of the absence of back mixing (Janssen et al., 2003). The photosynthetic efficiency can be increased significantly by increasing the gas flow rate ($\geqslant 0.05\ m\ s^{-1}$) leading to shorter light and dark cycle.

6.1.2. Airlift photobioreactor

Airlift reactors are vessel with two interconnecting zones. One of the tubes is called riser where gas mixture is sparged whereas the other region is called downcomer which does not receive the gas. Generally it exists in two forms internal loop and external loop. In internal loop reactor, regions are separated either by a draft tube or a split-cylinder while in external loop, riser and downcomer is separated physically by two different tubes. Mixing is done by bubbling the gas through sparger in the riser tube without any physical agitation. Riser is similar to bubble column where sparged gas moves upward randomly and haphazardly. This decreases the density of the riser making the liquid to move upward. This upward movement is assisted by the gas hold up of riser. In the disengagement zone gas leaves the liquid and its performance depends upon design of this section and the operating conditions. The amount of gas which does not disengage in the disengagement zone gets trapped by liquid moving downward in the downcomer. Gas hold up in the downcomer has a significant influence in the fluid dynamics of the airlift reactor. Degassed liquid moves downwards in the annular space in laminar fashion with defined and oriented motion. Increasing the gas hold-up difference between riser and downcomer is important criteria to take into account while designing airlift reactor. Airlift reactor has characteristics advantage of creating circular mixing pattern where liquid culture passes continuously through dark and light phase giving flashing light effect to algal cells (Barbosa et al., 2003). Residence time of gas in various zone controls performance affecting parameters like gas–liquid mass transfer, heat transfer, mixing and turbulence (Chisti and Young, 1993). It has been modified into many shapes like putting sparger into annular tube. Rectangular airlift photobioreactor is also suggested having better mixing characteristics and also the high photosynthetic efficiency but the disadvantage is its complexity and difficulty in scale-up (Janssen et al., 2003). An airlift photobioreactor with external loop has been designed by Loubiere et al. (2009) which produces swirling motion.

6.2. Flat panel photobioreactor

The flat panel reactor has cuboidal shape with minimal light path. It can be made from transparent materials like glass,

Plexiglass, polycarbonate. It is characterized by high surface area to volume ratio and open gas disengagement systems. Agitation is provided either by bubbling air from its one side through perforated tube or by rotating it mechanically through motor. A flat panel was built up by Barbosa et al. (2005) from lexan (polycarbonate) held together in stainless steel having surface to volume ratio of 0.34 cm^{-1}.The mixture of CO_2 and air was sparged through 17 needles with a diameter of 0.8 mm pinched through a piece of silicon placed at the bottom of the reactor. The reactor was illuminated at one surface with 10 fluorescent tubes having total light intensity of approximately 1000 μmol photons m^{-2} s^{-1} (Barbosa et al., 2005). It was modified by Zhang et al. (2001) by inclusion of baffles to improve agitation. Iqbal et al. (1993) modified flat panel reactor by including some more engineering features like giving it V shape to achieve high mixing rate, eliminating escape corners which minimizes shear stress and cell adhesion to the walls of the reactor. Tredici and Zittelli (1998) designed near horizontal flat panel which was divided longitudinally into five channels with two plexiglass manifolds at the top and at the bottom. Surface area to volume ratio was 40 m^{-1} with gas hold up capacity of 10.3%. Carbon dioxide gas mixture was injected axially through the bottom tubular Plexiglass manifolds. It had photosynthetic efficiency of 4.8% less compared to near horizontal tubular reactor (5.6%) when kept outdoor using *Arthrospira (Spirulina) platensis* M2 (Tredici and Zittelli, 1998). It may be due to that curved surface of later, which reduces the light saturation effect at midday. In a continuous culture of *Chlorella sorokiniana* using flat panel having short path length under high irradiance condition volumetric productivity obtained was 12.2 g $L^{-1}d^{-1}$. It was highest productivity of green algae so far discovered under over-saturating light condition (Cuaresma et al., 2009). It can be scaled up by arranging several plates over an area. Lengthening the reactor is not recommended by Zhang et al. (2002) for scale-up rather increase in liquid height and widening the light path is the recommended solution of scale-up. Flat panel designed by Degen et al. (2001) had the airlift mode of circulation. It had smaller downcomer zone and large riser zone where compressed air was injected. In addition, baffles were the other features of their reactor which was attached alternatively to the front and back of the larger faces of the panel. Transparent cooling jacket was also attached on the front illuminated side of the reactor. Volumetric mass productivity was 1.7 times higher than a similar bubble column reactor.

6.3. Horizontal tubular photobioreactor

Horizontal tubular reactors are placed horizontally giving the design of parallel set of tubes, loop shape, α shape, near horizontal tubular shape or horizontal tubular reactor. Its shape gives advantage in outdoor culture for their orientation towards sunlight resulting in high light conversion efficiency. CO_2 gas mixture is introduced into the tube connection via a dedicated gas exchange system. Oxygen build up during photosynthesis causes photo bleaching and reduces the photosynthetic efficiency (Miron et al., 1999). Methods adapted for cooling of the system has been spraying water on the surface of the tubes, overlapping of tubes, placing the light harvesting unit inside a pool of temperature controlled water, and regulating the temperature of feed or recirculation stream. Another major drawback is the high energy consumption of about 2000 W m^{-3} compared with ca. 50 W m^{-3} for bubble column and flat plate photobioreactors. This high energy input is necessary to reach high linear liquid velocities of about 20–50 ms^{-1} for achieving turbulent conditions with sufficient short light/dark cycles (Posten, 2009). The near horizontal tubular is similar to the horizontal tubular reactor however; it has inclination of few degrees towards the sun. This inclination helps in harnessing sun light more efficiently. Reactor designed by Tredici and Zittelli (1998) was made up of plexiglass tubes having 3.4 cm internal diameter placed side by side without any space between tubes. Tubes were connected at top and bottom ends by tubular plexiglass manifolds. It was laid on a wooden framework facing south with an angle of 5° horizontally (Tredici and Zittelli, 1998). Surface to volume ratio and gas holdup was 70 $m^{-1}$and 10.3%, respectively. Automatic evaporative cooling system was used for maintaining the temperature control. Volumetric productivity and photosynthetic efficiency was higher than flat reactor. Volumetric output achieved in this type of reactor was 1.26 g L^{-} d^{-1} by using *Arthrospira (Spirulina) platensis* M2 (Tredici and Zittelli, 1998).

6.4. Helical type photobioreactor

Helical type photobioreactor consists of coiled transparent and flexible tube of small diameter with separate or attached degassing unit. A centrifugal pump is used to drive the culture through long tube to the degassing unit. Travieso et al. (2001) experimented with this system with different algal strains. CO_2 gas mixture and feed can be circulated from either direction but injection from bottom gives better photosynthetic efficiency (Morita et al., 2001). Tredici and Zittelli (1998) designed coiled type photobioreactor with PVC having 3 cm diameter wound on a rigid vertical structure with an inclination of 2° with horizontal. It was provided with degasser to remove the produced oxygen and remaining residual gas of injected gas stream. Volumetric productivity and photosynthetic efficiency was found to be 0.9 g L^{-1} d^{-1} and 6.6%, respectively. Light dilution effect, use of diffusive radiation plus light absorbing capacity of PVC are responsible for its higher photosynthetic efficiency. It had surface area to volume ratio of 53 m^{-1} with 23% of total volume was occupied by the gas bubbles (Tredici and Zittelli, 1998). Its advantage included long tubes placed at small rise occupying small ground area, better CO_2 transfer from gas phase to liquid phase due to large CO_2 absorbing pathway (Watanabe et al., 1995). Although scale-up can be done simply adding of light harvesting unit but the energy required by centrifugal pump in recirculating the culture and associated shear stress limits its commercial use. Fouling on the inside of the reactor as experienced by the authors is another disadvantage of this system. Morita et al. (2000) gave the cone shape to the helical photobioreactor with a cone angle of 60°. The angle and height are strictly defined for conical helical system. Conical helical reactor was made-up of PVC tubing coiled in a conical framework. Air pump was used for the recirculation of the liquid. This system was also having attached degassing system and heat exchanger to control the temperature. At an angle of 60° photo-receiving area and hence photosynthetic productivities increases by a factor of two. Photosynthetic efficiency of 6.84% was greatest among all other cone angle tested for this reactor. Direction of injection of gas was tested from either direction with 10% (v/v) CO_2 and maximum photosynthetic efficiency of 6.25% was found (PAR) when gas was circulated through bottom of this reactor. The main advantage of cone shape is the light harvesting efficiency with the same basal area (Watanabe and Hall, 1996). Photobioreactor has advantage with respect to balance between energy input and photosynthetic efficiency. Less energy requirement for its operation and less mechanical stress imposed to algal cells are the other advantages of this reactor. Increasing the number of light harvesting units was the only way for scale-up because of its defined angle and size but it leads to larger energy loss in the complicated branches of the flow networks.

6.5. Stirred tank photobioreactor

Stirred tank reactor is most conventional where agitation is provided mechanically with the help of impeller of different sizes and shapes. Baffles are used in order to reduce vortex. CO_2 enriched air

is bubbled at the bottom to provide carbon source for the growth of algae. This type of bioreactor has been turned into photobioreactor by illuminating it externally by fluorescent lamps or optical fibres but the main disadvantage of this system is low surface area to volume ratio which in turn decreases light harvesting efficiency. Pohl et al. 1988 tried to solve the problem of availability of light to the culture by illuminating it internally by fluorescent lamps. Use of optical fibres has been also tried but the use of optical fibres for illumination has disadvantage because of its hindrance in the mixing pattern. New Brunswick Bioflo 115 and Bioengineering fermentors are commercially available having external light systems. Large disengagement zone separates the unused sparged gas and produced oxygen during photosynthesis from gassed liquid to gas phase. Low surface area to volume ratio and high shear stress imposed due to mechanical agitation limits its use in CO_2 sequestration.

6.6. Hybrid type photobioreactor

Hybrid type of photobioreactor is widely used which exploits the advantages of the two different type of reactor and one overcomes the disadvantage of other. Fernandez et al. (2001) has used integrated airlift system and external tubular loop placed horizontally in a thermostatic pond of water. Reactor had total volume of 200 litres. On one hand external loop acts like light harvesting unit as it gives high surface area to volume ratio and controls the temperature of the culture. On the other hand airlift system acts as a degassing system where probes can also be integrated in order to regulate the other culture variables. Hydrodynamics of airlift portion of the reactor was also used to control the flow velocity through the solar receiver. Its advantage includes better control over culture variables, enabling higher productivities and reducing power consumption (Fernandez et al., 2001). Grima et al. (1994) and Richmond et al. (1993) have developed similar type of integrated system but the external light harvesting unit of former was horizontal parallel sets of tubes different from loop like structure developed by later. Temperature was controlled by former using spray of water over the external light harvesting unit. Advantage of horizontal tubes was its photosynthetic efficiency and the low cost. The main disadvantage was large occupied land area and very narrow light harvesting unit. It is not economically feasible because of the cost associated with required land area and bundle of tubes.

The α-shaped reactor is another type of hybrid system developed by Lee et al. (1995) and designed and constructed based on algal physiology and sunlight. In this reactor, the culture is lifted 5 m by air to a receiver tank and culture flows down an inclined PVC tube (2.5 cm ID × 25 m) making 25° with the horizontal to reach another set of air riser tubes and the process repeated for the next set of tubes. The unidirectional and high liquid flow rate can be achieved at relatively low air flow rates. Also due to large area to volume ratio, photosynthetic efficiency is high. It was reported that the biomass concentration was around 10 gdw L^{-1} (Lee et al., 1995).

7. Promising photobioreactors

Vertical tubular, helical tubular and flat panel reactors have edge over other reactors when considering of photosynthetic efficiency, degree of control, land requirement and scale-up (Carvalho et al., 2006). Fouling inside the helical reactor and the fluctuation in the hydrodynamic stress are the common problem associated with this reactor. Among the different photobioreactors available for CO_2 sequestration, airlift reactor seems the most suitable reactor for CO_2 sequestration from the flue gas. High gas transfer, uniform mixing, low hydrodynamic stress, ease of control are the characteristics advantages of this reactor. Integrating a tubular loop reactor with airlift will compensate the disadvantage of limited S/V ratio and scalability of airlift photobioreactor.

8. Conclusions

CO_2 sequestration process requires detail knowledge of flue gas and biology of cells. Major factors affecting this process can be temperature, pH, SO_x and NO_x, light, culture strain, culture density, critical CO_2 concentration, CO_2 mass transfer and O_2 accumulation. Cultivation of algae also requires developing a suitable photobioreactor having features like higher S/V ratio, mixing, mass transfer, scalability and ease of operation. None of the single photobioreactor is good enough to have all the merits. Airlift reactor seems the most promising for the CO_2 sequestration. However, integrated type of reactor will help in ease of scalability.

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