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Algal mediated Carbon Sequestration to Mitigate the Climate Change

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Abstract- The global carbon cycle has altered significantly due to extensive use of fossil fuels which lead to increase in the emission of greenhouse gases such as CO_2, CH_4, NO_2 and CFCs causing climate change. In order to achieve environmental and economic sustainability, a renewable, carbon neutral fuels are required that are also capable of sequestering atmospheric carbon dioxide. Amongst various carbon sequestration technologies, the biological methods particularly the ones using microalgae, have several merits. This include, direct CO_2 capture and fixation from flue gases by suitable micro-algal strains and their biomass conversion into useful products. This is quite important because the separation of CO_2 from flue gases takes a major portion over 70% of the total sequestration cost. Microalgae have ability to fix CO_2 using solar energy with efficiency 10 times greater than the terrestrial plants with numerous additional technological advantages. They have comparatively higher growth rate, allowing a large quantity of biomass production in a shorter amount of time in a smaller area. In addition carbon fixed by microalgae is incorporated into carbohydrates and lipids, so that energy, chemicals or food can be produced from algal biomass. Microalgae have a huge potential to capture CO_2 from power plants, steel, cement, oil, automobiles and many other industries and the resulting algal biomass can be not only used for biofuel production but also for various economic products such as fertilizers and pharmaceuticals. The present review aimed at shedding some light upon the sequestration of CO_2 from stationary combustion systems by microalgal photosynthesis. It also discussed about the various types of microalgal production systems, factors that affect microalgal growth and the future directions for enhancing CO_2 mitigation.

Index Terms- Microalgae, climate change, mitigation, carbon sequestration, biofuel.

1. INCREASING CARBON IN THE ENVIRONMENT

Climate change is one of the major challenges of our time and adds considerable stress to our societies and to the environment. The impacts of climate change are global in scope and unprecedented in scale. Without drastic action today, adapting to these impacts in the future will be more difficult and costly.

The increasing concentration of carbon dioxide (CO_2) in the atmosphere is considered to be one of the main causes of the global warming problem. Demand for energy and associated services, to meet social and economic development and improve human welfare and health, is increasing. All societies require energy services to meet basic human needs (e.g., lighting, cooking, space comfort, mobility and communication) and to serve productive processes. Since approximately 1850, global use of fossil fuels (coal, oil and gas) has increased to dominate energy supply, leading to a rapid growth in carbon dioxide (CO_2) emissions. These use of fossil fuels results in the emission of Greenhouse Gases such as Carbon dioxide (76%), Methane (13%), Nitrous oxide (6%) and Fluorocarbons (5%). Out of these gases carbon dioxide is the major culprit to cause climate change. According to IPCC report the average concentration of CO_2 increased from 315 ppm in 1960 to >380 ppm in 2007 [1]. There has been a 35% increase in CO_2 emission worldwide since 1990 (Fig.1).

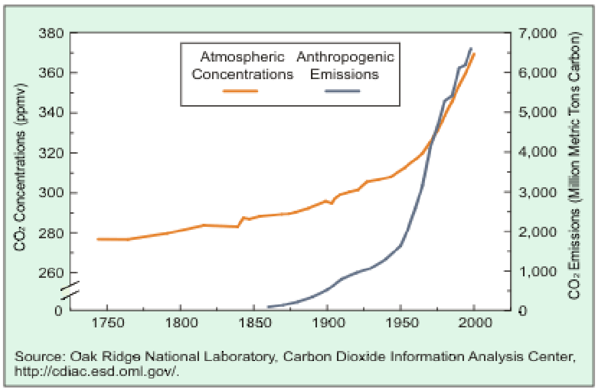

Fig.1-Trends in Atmospheric Concentrations and Anthropogenic Emissions of CO_2

About three-quarters of human-made carbon dioxide emissions were from burning fossil fuels since large-scale industrialization began around 150 years ago.

Concentrations of carbon dioxide in the atmosphere are naturally regulated by numerous processes collectively known as the "carbon cycle" (Fig.2). The movement (flux) of carbon between the atmosphere and the land and oceans is dominated by natural processes, such as plant photosynthesis. While these natural processes can absorb some of the net 6.1 billion metric tons of anthropogenic carbon dioxide emissions produced each year (measured in carbon equivalent terms), an estimated 3.2 billion metric tons is added to the atmosphere annually and the remainder is found in various terrestrial and oceanic sinks [1].The Earth's positive imbalance between emissions and absorption results in the continuing growth in greenhouse gases in the atmosphere. These greenhouse gases (GHGs) cause depletion of ozone layer protecting the atmosphere against UV radiation, thereby warming the atmosphere and leading to climate change.

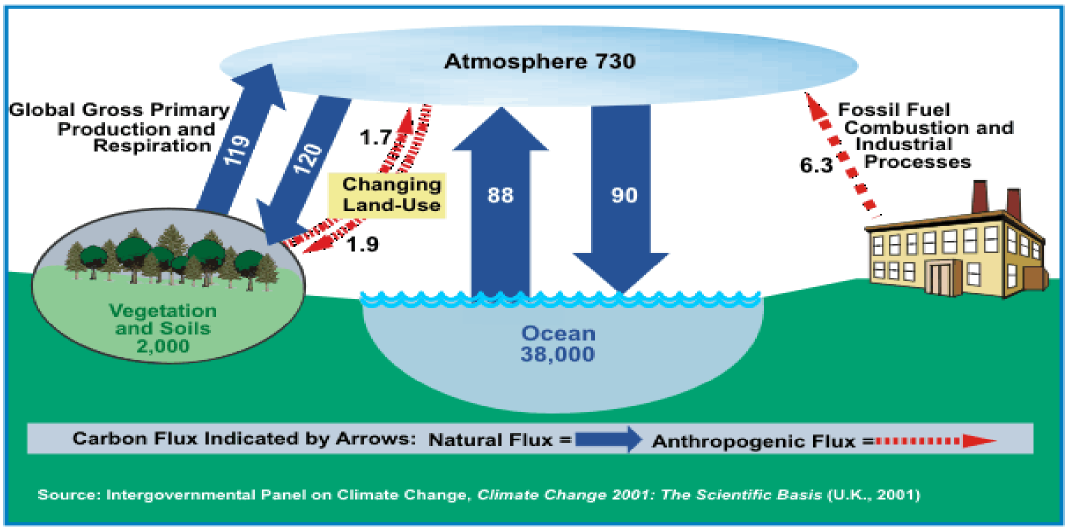

Fig.2-Global Carbon Cycle (Billion Metric Tons Carbon)

The United Nations promoted the Kyoto Protocol (1997) with the objective of reducing greenhouse gases by 5.2% on the basis of the emission in1990, and more than 170 countries have ratified the protocol. Therefore, in order to achieve environmental and economic sustainability, the future fuel production processes need to be not only renewable but also capable of reducing atmospheric carbon dioxide. So, a shift from fossil fuels to low carbon fuels becomes the highest priority. The most effective ways to reduce CO_2 emission is to improve the energy efficiency of each economic sector and to reduce the cutting of tropical and temperate forest around the world. These methods however may not be able to control CO_2 emissions due to various political and socio-economic barriers, so other more innovative and less well defined CO_2 mitigation measures are required. Selecting the most appropriate technology to limit the amount of carbon dioxide entering the atmosphere has been the major focus of research. This has led to increased interest in a new strategy termed carbon capture and storage, or sequestration.

2. CARBON SEQUESTRATION

Carbon sequestration is the capture of carbon dioxide (CO_2) and may refer specifically to "**The process of removing carbon from the atmosphere and depositing it in a reservoir**" [2]. Carbon sequestration describes long-term storage of carbon dioxide or other forms of carbon to either mitigate or defer global warming and avoid dangerous climate change. It has been proposed as a way to slow the atmospheric and marine accumulation of greenhouse gases, which are released by burning fossil fuels.

Available technologies for CO_2 removal/capture include physicochemical absorbents, injection into deep oceans and geological formations, and enhanced biological fixation (or mitigation). Adsorbent materials (e.g. LiOH) are typically non-renewable and require significant space for storage. Other abiotic methods are based on direct injection of CO_2 into the deep ocean, geological strata, old coal mines, oil wells or saline aquifers, as well as mineral carbonation of CO_2. These methods present significant challenges, including high space requirements and potential CO_2 leakage over time [3]. And also these are expensive options (potentially more than doubling the cost of electrical generation via fossil fuels) with no opportunity for profit to displace the cost [4]. Hence, biological mitigation is the only economically feasible and environmentally sustainable technology in the long term.

Biological mitigation method comprises actions that follow three strategies: (i) conservation of existing carbon pools, (ii) sequestration by increasing the size of carbon pools, and (iii) substitution of non-renewable resources for low impact biological products. The most practical of these methods is to increase CO_2 sinks through photosynthesis including increased carbon storage in standing tree biomass, substitution of fossil fuels with biofuels, increase in soil carbon sequestration and increase in soil primary productivity.

Biological carbon sequestration

Global carbon cycling is dominated by the paired biological processes of photosynthesis and respiration. Photosynthetic plants and microbes of Earth's landmasses and oceans use solar energy to transform atmospheric CO_2 into organic carbon. The majority of this organic carbon is rapidly consumed by plants or microbial decomposers for respiration and returned to the atmosphere as CO_2. Coupling between the two processes results in a near equilibrium between photosynthesis and respiration at the global scale, but some fraction of organic carbon also remains in stabilized forms such as biomass, soil, and deep ocean sediments. This process, known as carbon bio-sequestration, temporarily removes carbon from active cycling and has thus far absorbed a substantial fraction of anthropogenic carbon emissions.

Biological fixation of CO_2 is an attractive option because plants naturally capture and use CO_2 as a part of the photosynthetic process. Terrestrial plants sequester vast amounts of CO_2 from the atmosphere However, because of the relatively small percentage of CO_2 in the atmosphere (approximately 0.036%), the use of terrestrial plants is not an economically feasible option. Bio-fixation of CO_2 using microalgae has emerged as a potential option. Microalgae have the advantages of efficient photosynthesis superior to C_4 plants (those plants that form four carbon stable intermediates in the photosynthetic process; generally associated with agricultural and large terrestrial plants), fast proliferation rates, wide tolerance to extreme environments, and potential for intensive cultures. These advantages promise high performance in the reduction of CO_2.

Microalgae can be extensively used to capture CO_2 from stationary combustion sources like power plants [5,6,7], steel, cement, oil, automobiles and many other industries and the resulting algal biomass can be not only used for biofuel production but also for various industrial products. Besides giving environmental and economic benefit, large scale algae cultivation can create millions of jobs at different levels of the society.

3. CARBON SEQUESTRATION BY ALGAE

3.1 Biochemistry of CO_2 fixation

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

$$CO_2 + H_2O + \text{Light} \longrightarrow (CH_2O)_n + O_2$$

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 [8]. 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 [9].

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 ppm) 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% [10]. 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. CCM acts as an enhancer for higher growth rates in algae and hence can be used for improvement in algal biomass productivity [11]. The expression of the enzyme carbonic anhydrase has been associated with induction of the CCMs. Carbonic anhydrase 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 [12].

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

We may conclude from the above that the majority of the microalgae have developed solutions in time to adapt to limited concentrations of atmospheric CO_2, respectively to relatively low concentrations of species of dissolved inorganic carbon (DIC) present in the water environment.

The use of microalgae cultures to sequestrate the CO_2 emissions is supposed to follow a different scenario, in which a much higher CO_2 concentration is needed as an essential condition for this application. A small percentage increase in carbon dioxide during the process of airing is a common practice to obtain a higher rate in the growth of cultures.

If a microalgae strain growing in a concentration of 0.033% CO_2 in the air it becomes obvious that under proper light conditions (proper for the photosynthesis), the phototrophic growth shall be limited due to the low concentration of carbon dioxide. Considering that all the carbon dioxide is fully accepted into the biomass, having a carbon content of 50%, a very small value productivity of 3.54×10^{-4} g biomass/minute is obtained. Productivity improves if we increase the CO_2 in the gas flow; this level is recommended by the majority of authors [13,14,15,16,17].

The relatively high content of CO_2 in flue gas (approximately 10-15% compared to the 350 ppm in ambient air) has been shown to significantly increase growth rates of certain species of microalgae. Therefore, this application is ideal for contained system, engineered to use, specially selected strains of microalgae to maximize CO_2 conversion to algal biomass and thus not emitting the greenhouse gas to the atmosphere. In this case, the algal biomass represents a natural sink for carbon sequestration.

3.2 Potential algal species for CO_2 fixation

To realize workable biological CO_2 fixation systems, selection of optimal algae species is vital. The selection of optimal algal species depends on specific strategies employed for CO_2 sequestration. CO_2 fixation by photoautotrophic macro-algae and microalgae growing in aquatic environments has the potential to diminish the release of CO_2 into the atmosphere, helping alleviate the trend toward global warming.

3.2.1 Macro-algae

Macro-algae or "seaweeds" are multicellular plants growing in salt or fresh water. They belong to the lower plants, meaning that they do not have roots, stems and leaves. Instead they are composed of a thallus (leaf-like) and sometimes a stem and a foot. Some species have gas-filled structures to provide buoyancy. They are often fast growing and can reach sizes of up to 60 m in length [18].

They are classified into three broad groups based on their pigmentation: i) brown seaweed (Phaeophyceae); ii) red seaweed (Rhodophyceae) and iii) green seaweed (Chlorophyceae). Seaweeds are mainly utilized for the production of food and the extraction of hydrocolloids.

In their natural environment, macro-algae grow on rocky substrates and form stable, multi-layered, perennial vegetation capturing almost all available photons. Due to the fact that seaweeds are fixed to their substrate, values for maximum productivity may be 10 times higher for a seaweed stand than for a plankton population. The productivity of plankton is much lower because most of the photons are absorbed or scattered by abiotic particles, and the algae are so thinly distributed.

Approximately 200 species of seaweeds are commercial used worldwide, few of which are intensively cultivated, such as the brown algae *Laminaria japonica* and *Undaria pinnatifida*, the red algae *Porphyra, Eucheuma, Kappaphycus* and *Gracilaria*, and the green algae *Monostroma* and *Enteromorpha* [19].

3.2.2 Microalgae

Microalgae are microscopic organisms that grow in salt or fresh water. These organisms constitute a polyphyletic and highly diverse group of prokaryotic (two divisions) and eukaryotic (nine divisions) organisms. The classification into divisions is based on various properties such as pigmentation, chemical nature of photosynthetic storage product, the organisation of photosynthetic membranes and other morphological features. The three most important classes of micro-algae in terms of abundance are the diatoms (Bacillariophyceae), the green algae (Chlorophyceae), and the golden algae (Chrysophyceae). In this review the cyanobacteria (blue-green algae) (Cyanophyceae) are also referred to as micro-algae.

Diatoms are the dominant life form in phytoplankton and probably represent the largest group of biomass producers on earth. It is estimated that more than 100,000 species exist. The cell walls of diatoms contain polymerized silica, and they often accumulate oils and chrysolaminarin. Green algae are especially abundant in fresh water. The main storage compound of these algae is starch, although oils can also be produced. The fresh water green algae *Haematococcus pluvialis* is commercially important as a source for astaxanthin, *Chlorella vulgaris* as a supplementary food product, and the halophilic algae *Dunaliella* species as a source of ß-carotene. The golden algae are similar to the diatoms and produce oils and carbohydrates. The blue-green algae (cyanobacteria) are found in a variety of habitats and are often known for their toxic water polluting products, for example *Spirulina* (*Arthrospira platensis* and *A. maxima*).

The photosynthetic mechanism of microalgae is similar to land based plants, but due to a simple cellular structure, and submerged in an aqueous environment where they have efficient access to water, CO_2 and other nutrients, they are generally more efficient in converting solar energy into biomass. Many microalgae species are able to switch from phototrophic to heterotrophic growth. As heterotrophs, the algae rely on glucose or other utilizable carbon sources for carbon metabolism and energy. Some algae can also grow mixotrophically.

Exploitation of micro-algae for bioenergy generation (biodiesel, biomethane, biohydrogen), or combined applications for biofuels production and CO_2-mitigation by which CO_2 is captured and sequestered, are under research [20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31].

The dominating species of micro-algae in commercial production includes *Isochrysis, Chaetoceros, Chlorella, Arthrospira (Spirulina)* and *Dunaliella* [32].

Table 1- Examples of some potential algal species

Macro-algae
Macrocystis, Laminaria, Fucus, Sargassum, Ascophyllum, Ulva, Porphyra, Palmaria, Enteromorpha etc.
Microalgae
Chlorella sp., *Synchocystis* sp., *Chlorococcum* sp., *Cyanadium caldarium, Coelastrum* sp., *Chorisystis* sp., *Monoraphidium griffithii, Scenedesmus* sp., *Euglena* sp., *Dunaliella* sp., *Spirogyra* sp., *Chlamydomonas* sp., *Spirulina* sp., *Prymnestium* sp., *Tetraselmis* sp., *Porphyridium* sp., *Synechoccus* sp., *Anabaena cylindrical* etc.

4. ALGAL PRODUCTION SYSTEM

Two distinctive cultural systems have been proposed for CO_2 sequestration with microalgae. One is the open pond system, and the other is the closed photobioreactor system. The vision of viable strategy for carbon sequestration based on the photosynthetic microalgae is shown conceptually in Fig 4. In this figure CO_2 from the fossil fuel combustion system and nutrient are added to a photobioreactor where microalgae utilize sunlight to photo-synthetically convert the CO_2 into biomass.

There is ongoing discussion regarding whether the open pond system or the closed photobioreactor system would be better for CO_2 sequestration [33]. Apparent advantages for utilizing the open pond system are low initial and operational costs. On the other hand, an advantage for the photobioreactor system has a higher potential productivity due to better environmental control and harvesting efficiency.

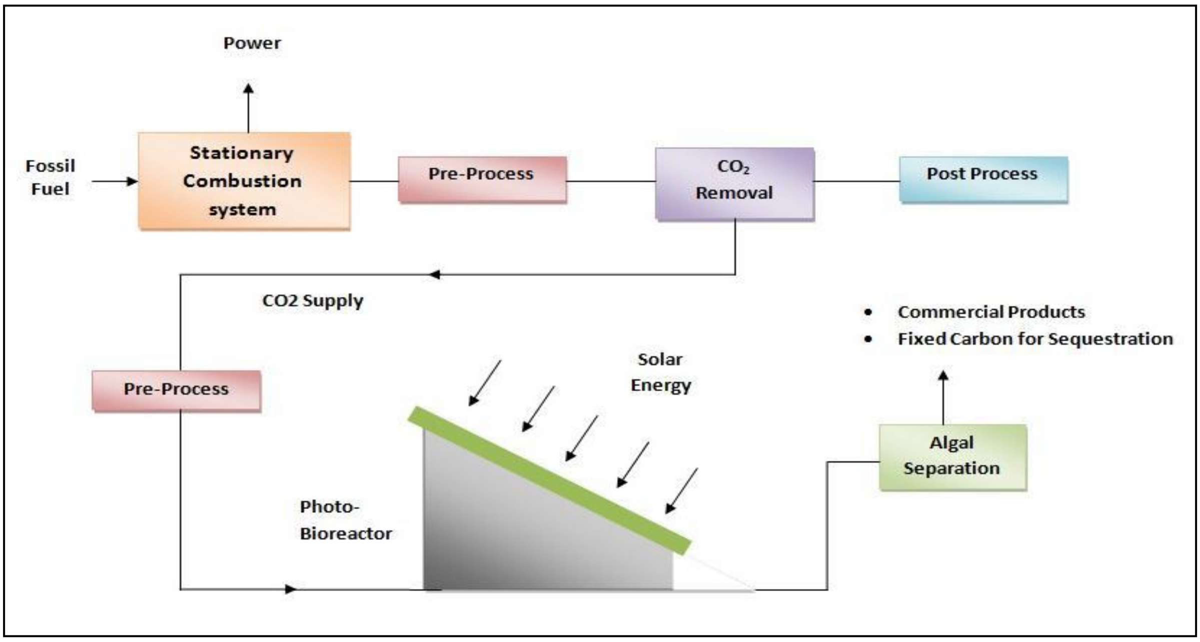

Fig.2- A simple concept for a microalgal-based carbon capture scheme

4.1 Open pond systems

Open pond systems are shallow (typically one-foot deep) ponds, from about one acre to several acres in size, in which the algae are exposed to natural solar radiation (sunlight) which they convert into biomass. Typically the ponds are called raceway ponds because their shape resembles a race track (Fig.3). They often use paddle wheels or other water moving devices to keep the algae circulating. Nutrients can be provided through runoff water from nearby land areas or by channeling the water from sewage/water treatment plants and some mixing can be accomplished by appropriately designed guides. Algal cultures can be defined (one or more selected strains), or are made up of an undefined mixture of strains.

4.2 Closed Photobioreactors

A photobioreactor (PBR) differs from an open pond in that the algae enclosed in a transparent vessel, which can be as simple as a greenhouse, but, more generally, is a tubular, bag-type or panel design, in many shapes and sizes, oriented vertically or horizontally (Fig.4).

Algae receive sunlight either directly through the transparent container walls or via light fibers or tubes that channel it from sunlight collectors. Some systems even use additional artificial light to help boost production, and a few rely exclusively on artificial lights. Algal cultures consist of a single or several specific strains optimized for producing the desired product. Water, necessary nutrients and CO_2 are provided in a controlled way, while oxygen has to be removed.

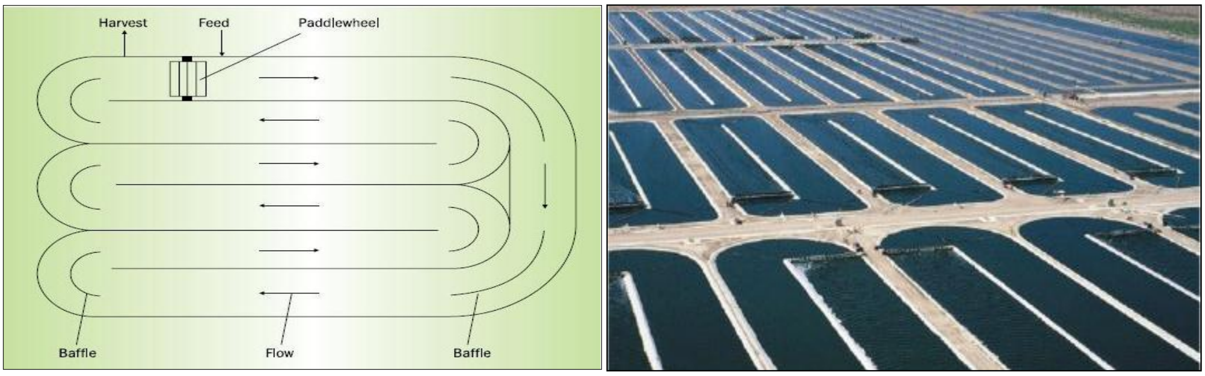

Fig.3- A raceway pond system

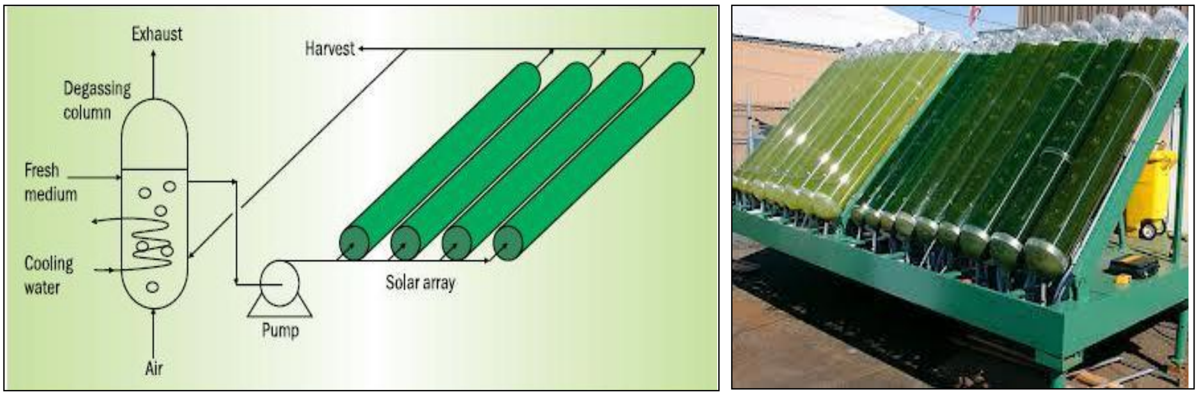

Fig. 4- A closed photobioreactor (PBR)

4.3 Comparison of the different production systems

The high capital cost associated with producing microalgae in closed culture systems is the main challenge for commercialization of such systems [34]. Open systems do not require expenses associated with sterilization of axenic algal cultures. However this leads to high risk of contamination of the culture by bacteria or other unwanted microorganisms. A common strategy therefore to achieve monocultures in an open pond system is to keep them at extreme culture conditions such as high salinity, nutrition or alkalinity (Lee 2001). Consequently, this strictly limits the species of algae that can be grown in such systems. To our knowledge, currently only *Dunaliella* (high salinity), *Spirulina* (high alkalinity) and *Chlorella* (high nutrition) have been successfully grown in commercial open pond systems [35].

The necessity for a large cultivation area has been pointed out as a limitation in using open ponds to grow microalgae for mitigating the CO_2 released from power generating plants. It has been estimated that a raceway pond requires 1.5 km^2 to fix the CO_2 emitted from a 150 MW thermal power plant [36]. The large area requirements are partly due to the comparable lower productivity of open pond13systems. It was pointed out that improving the control of limiting parameters in open ponds such as culture medium temperature and contamination and thereby increasing productivity could be accomplished by using a transparent cover over the ponds, such as a greenhouse [37].

Selection of a suitable production system clearly depends on the purpose of the production facility. A comparison of the different production systems is presented in Table 2.

Table 2- Comparison of different algal production systems

Parameter or issue	Open ponds and raceways	Photobioreactors (PBR)
Required space	High	For PBR itself low
Water loss	Very high, may also cause salt precipitation	Low
CO_2-loss	High, depending on pond depth	Low
Oxygen concentration	Usually low enough because of continuous spontaneous outgassing	Build-up in closed system requires gas exchange devices (O_2 must be removed to prevent inhibition of photosynthesis and photooxidative damage)
Temperature	Highly variable, some control possible by pond depth	Cooling often required (by spraying water on PBR or immersing tubes in cooling baths)
Shear	Low (gentle mixing)	High (fast and turbulent flows required for good mixing, pumping through gas exchange devices)
Cleaning	No issue	Required (wall-growth and dirt reduce light intensity), but causes abrasion, limiting PBR lifetime
Contamination risk	High	Low
Biomass quality	Variable	Reproducible
Biomass concentration	Low, between 0.1 and 0.5 g l-1	High, between 2 and 8 g l-1
Production flexibility	Only few species possible, difficult to switch	High, switching possible
Process control and reproducibility	Limited (flow speed, mixing, temperature only by pond depth)	Possible within certain tolerances
Weather dependence	Weather dependent	Medium (light intensity, cooling required)
Startup	6 – 8 weeks	2 – 4 weeks
Capital costs	High ~ US $ 100,000 per hectare	Very high ~ US $ 1,000,000 per hectare (PBR plus supporting systems)
Operating costs	Low (paddle wheel, CO_2 addition)	Very high (CO_2 addition, pH-control, oxygen removal, cooling, cleaning, maintenance)
Harvesting cost	High, species dependent	Lower due to high biomass concentration and better control over species and conditions
Current commercial applications	5000 t of algal biomass per year	Limited to processes for high added value compounds or algae used in food and cosmetics

5. FACTORS AFFECTING THE CO_2 SEQUESTRATION PROCESS

Microalgae utilize CO_2 as one of their main building blocks and we propose that algal photosynthesis may be a viable option for anthropogenic CO_2 capture and sequestration in the form of biomass and a variety of high value compounds. The most relevant environmental factors that affect the growth of microalgae include light, temperature, pH, salinity, nutrient qualitative and quantitative profiles, and dissolved oxygen (DO), as well as levels of toxic elements/compounds, such as heavy metals or synthetic organics. Biological factors that might constrain microalgal growth rates include predation, viruses, competition and growth of epiphytes [38]. Finally, microalgal growth can be affected by such reactor operating conditions as hydraulic residence time, harvesting rates, gas transfer and mixing equipment because they affect CO_2 availability, shear rates and light exposure.

5.1 Energy harvesting

Sunlight is the most common source of energy for microalgae, to an extent that is rather species-dependent. 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 proteins [39]. Although light intensity requirements of typical microalgae are relatively low compared with those of higher plants, microalgal activity usually rises, with increasing light intensity, up to 400 mmol m^{-2} s^{-1} [40].

5.2 Temperature effects

Temperature is one of the major factors that regulate cellular, morphological and physiological responses of microalgae: higher temperatures generally accelerate the metabolic rates of microalgae, whereas low temperatures lead to inhibition of microalgal growth [40]. The optimal temperature varies among microalgal species [41]. Optimal growth temperatures of 15–26°C have been reported for some species, with maximum cell densities obtained at 23°C.

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 3).

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.

Table 3- Temperature tolerance of various species

Algal species	**Maximum temperature tolerance (°C)**	**Refe-rences**
Cyanidium caldarium	60	[42]
Scenedesmus sp.	30	[43]
Synechococcus elongates	60	[44]
Chlorella sp.	45	[43]
Eudorina sp.	30	[43]
Chlamydomonas sp.	35	[45]
Nannochloris sp.	25	[46]
Monoraphidium minutum	25	[47]

5.3 pH effect

Most microalgal species are favored by neutral pH, whereas some species are tolerant to higher pH, e.g. *Spirulina platensis* at pH 9 [48] or lower pH, e.g. *Chlorococcum littorale* at pH 4 [49]. There is a complex relationship between CO_2 concentration and pH in microalgal bioreactor systems, owing to the underlying chemical equilibria among such chemical species as CO_2, H_2CO_3, $HCO_3^-$and CO_3^{2-}. Increasing CO_2 concentrations can lead to higher biomass productivity, but will also decrease pH, which can have an adverse effect upon microalgal physiology. By contrast, microalgae have been shown to cause arise in pH to 10–11 in open ponds because of CO_2 uptake [50]. This increase in pH can be beneficial for inactivation of pathogens in microalgal wastewater treatment, but can also inhibit microalgal growth.

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 [51]. 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.

5.4 CO_2 concentration

Biological CO_2 fixation can be carried out by higher plants and microalgae, yet the latter possess a greater ability to fix CO_2 [52, 27, 53]. Usual sources of CO_2 for microalgae include: (i) atmospheric CO_2; (ii) CO_2 from industrial exhaust gases (e.g. flue gas and flaring gas); and (iii) CO_2 chemically fixed in the form of soluble carbonates (e.g. $NaHCO_3$ and Na_2CO_3). The tolerance of various microalgal species to the concentration of CO_2 is variable.

Atmospheric CO_2 levels 0.0387% (v/v) are not sufficient to support the high microalgal growth rates and productivities needed for full-scale biofuel production. Waste gases from combustion processes, however, typically contain >15% (v/v) CO_2; this percentage indicates, in principle, that combustion processes will provide sufficient amounts of CO_2 for large-scale production of microalgae.

In aquous environment dissolved CO_2 always exist in equilibrium with H_2CO_3, HCO_3^- and CO_3^{2-} which concentration depends upon pH and temperature. Due to fast interconvertible reaction among them, consumption of any of inorganic 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 [54].

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 higherCO_2 concentration which causes biological reduction in the capacity of algal cells for CO_2 sequestration [55]. 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 increasing CO_2% (v/v) in the gas mixture up to certain percentage beyond which productivity decreases (Table 4).

Table 4- CO_2 tolerance of various species

Algal species	Maximum CO_2 % (v/v) tolerance	Refe-rences
Cyanidium caldarium	100 %	[42]
Scenedesmussp.	80 %	[43]
Chlorococcum littorale	60 %	[49]
Synechococcus elongates	60 %	[44]
Euglena gracilis	45 %	[56]
Chlorella sp.	40 %	[43]
Eudorina sp.	20 %	[43]
Dunaliella tertiolecta	15 %	[57]
Chlamydomonas sp.	15 %	[45]
Nannochloris sp.	15 %	[46]
Tetraselmis sp.	15 %	[58]

5.5 O_2 accumulation

Photosynthesis is a reversible set of reactions, and excessive dissolved oxygen, DO (i.e. >35 mg/l), can inhibit the metabolic processes [54]. 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 [59].

5.6 Nutrient requirements

Apart from carbon, nitrogen is the most important element that is required for microalgal nutrition [60] and, as a constituent of both nucleic acids and proteins, nitrogen is directly associated with the primary metabolism of microalgae. Fast-growing microalgal species prefer ammonium rather than nitrate as a primary nitrogen source [61]; intermittent nitrate feeding, however, will enhance microalgal growth if a medium that lacks nitrate is used [62].

Phosphorus is the third most important nutrient for microalgal growth, and should be supplied to significant excess as phosphates because not all phosphorus compounds are bioavailable (e.g. those combined with metal ions) [63]. In the case of marine microalgae, seawater supplemented with commercial nitrate and phosphate fertilizers is commonly used for production of microalgae [61]. Nevertheless, trace species, such as metals (Mg, Ca, Mn, Zn, Cu and Mb) and vitamins, are typically added for effective cultivation [60].

5.7 Toxic compounds

Elements and compounds that may be toxic to microalgae include heavy metals and various gases, such asCO_2, NO_x, SO_x, O_2 and NH_3. The trace acid gases (NO_x & SO_x) can be effectively used as nutrients for microalgae [51, 64].

5.8 Biotic factors

Biotic factors including pathogens, growth of epiphytes, predation and competition by other algae and may also affect the algal growth [38].

5.9 Operational factors

Operational factors such as: shear produced by mixing, dilution rate, depth and harvest frequency also play important role in algal growth. Proper mixing helps in the uniform mixing of nutrient and also in the better distribution of light over cells. Low mixing rates hamper gaseous mass transfer and might even permit biomass settling. Some time it leads to emergence of stagnant zones, where light and nutrients are insufficiently available and anoxic/anaerobic conditions will thus prevail, which results in a decrease of productivity. Culture viability might also be compromised by production and accumulation of toxic compounds in stagnant zones [60]. Conversely, high mixing rates can cause shear damage to cells [38], besides requiring a large energy input.

6. ADVANTAGES OF ALGAL BASED CARBON SEQUESTRATION

6.1 Efficient CO_2 capturing

The carbon biological sequestration, in particular the use of technologically adequate photosynthetic strains may be one of the most promising methods for the reduction of the CO_2emissions in the energy sector, both from the cost and from the environment points of view. Microalgae are able to capture anthropogenic CO_2 under a wide variety of pH and gas concentrations. The efficiency of CO_2 capture by microalgae is directly dependent on the pH of the culture but is not affected by differences in gas composition. The biomass productivity increases with increase in CO_2 concentration up to certain percentage beyond which productivity decreases. For example, CO_2sequestration experiment 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 (Table-5). However, the sequestration of CO_2 from flue gas emitted by coal fired thermal power plant confirms that C*hlorella* 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. It is concluded that pre-adaptation of cells with lower percentage of CO_2concentration leads the tolerability of cells in higher percentage of CO_2 [51].

Table 5- Carbon sequestration capabilities of different algal species

Algal species	% CO_2 at influent (% v/v)	% CO_2 sequestered	Amount of CO_2 sequestered (gh^{-1})	Maximum biomass production (gL^{-1})	Biomass productivity (mg dwt L^{-1} d^{-1})	CO_2 fixation rate
Chlorella sp.	Air	-	-	0.682 ± 0.007	-	-
	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	-	-
Scenedesmus obliquus	10	-	-	3.13	217.50 ± 11.24	-
	5.5 (flue gas)	24	-	-	203	-
Botrycoccus braunii	6	53.29	-	-	26.55 ± 7.66	-
	12	45.61	-	-	77	-
Spirulina sp.	6	53.29	-	-	220	-
	12	45.61	-	3.5	-	-
Synechocyatis aquatilis	10	-	-	-	30 g m^{-2} day^{-1}	50 g m^{-2} day^{-1}
Anabaena sp.	Air	-	-	-	0.31 g m^{-2} day^{-1}	1.45 g m^{-2} day^{-1}
Phaeodactylum tricornutum	60			6.2		2.45 g m^{-2} day^{-1}

(Source: [63])

6.2 Major products

Microalgae are fast growing photoautotrophic organisms, which can transform CO_2 into the biomass. Algal biomass has relatively high lipid, carbohydrates and nutrient contents (Table 6), thus they are the excellent source for biofuels such as biodiesel, bioethanol and biomethane; as well as a number of valuable pharmaceutical and nutraceutical products.

Table 6- Protein, carbohydrate and oil contents of microalgae

Proteins and carbohydrates contents of microalgae

Algal Strain	Protein (% dwt)	Carbohydrate (% dwt)
Scendesmus obliquus	50-56	10-17
Scenedesmus quadricauda	47	-
Scenedesmus dimorphus	8-18	21-52
Chlamydomonas rheinhardii	48	17
Chlorella vulgaris	51-58	12-17
Chlorella pyrenoidosa	57	26
Spirogyra sp.	6-20	33-64
Dunaliella bioculata	49	4
Dunaliella salina	57	32
Euglena gracilis	39-61	14-18
Prymnesium parvum	28-45	25-33
Tetraselmis maculate	52	15
Porphyridium cruentum	28-45	40-57
Spirulina platensis	52	8-14
Spirulins maxima	28-39	13-16
Synechoccus sp.	46-63	15
Anabaena cylindrical	43-56	25-30

Oil content of microalgae

Algal Strain	Oil content (% dwt)
Botryococcus braunii	25-75
Chlorella sp.	28-32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16-37
Dunaliella primolecta	23
Isochrysis sp.	25-33
Monallanthus salina	>20
Nannochloris sp.	20-35
Nannochloropsis sp.	31-68
Neochloris oleoabundans	35-54
Nitzschina sp.	45-47
Phaeodactylum tricornutum	20-30
Schizochytrium sp.	50-77
Tetraselmis suecica	15-23

(Adapted from: [60,27])

Bioenergy from microalgal products includes: (i) biogas produced via anaerobic digestion or co-digestion of microalgal biomass (e.g. with sewage sludge); (ii) electricity through direct biomass combustion or indirectly via combustion of the biogas derived from microalgae; (iii) biodiesel after oil extraction and re-esterification with small-chain monoalcohols; (iv) ethanol through fermentation; and (v) liquid fuels via thermochemical conversions, such as pyrolysis, gasification or liquefaction. Most bioenergy studies that pertain to microalgae have focused on biodiesel production.

Industrial chemicals extracted from microalgae include: (i) glycerol, which is widely employed in food and personal care products; (ii) astaxanthin and other carotenoids, used as antioxidants and coloring agents in food, cosmetics and aquaculture; (iii) fatty acids, used in cosmetics; (iv) poly-ß-hydroxybutyrate, used in plastics; and (v) polysaccharides, such as agar, alginates and carrageenans, which are employed as thickening agents for foods. Several recent reviews have focused on the isolation of health-promoting biomolecules from microalgae (e.g. polyunsaturated fatty acids).

6.3 Waste water treatment

Microalgae can utilize low-quality water, such as agricultural runoff or municipal, industrial or agricultural waste waters, as a source of water for the growth medium as well as a source of nitrogen, phosphorus and minor nutrients. Hence, an additional economic and environmental incentive exists as a result of the decreased cost of water and chemicals required for the formulation of the growth medium, while providing a pathway for waste water treatment. Although the most common application of microalgae in wastewater treatment aims at nutrient removal/recovery, microalgae have also been utilized for removal of heavy metals and organic matter; the latter requires heterotrophic metabolism. A consortium of microalgae and bacteria has been used to biodegrade black oil and detoxify industrial waste water. Biogas production can be accomplished through digestion of microalgae or co-digestion of microalgae and sewage sludge. Finally, secondary utilization of microalgae has been successful in toxicity monitoring.

7. CONCLUSION

The carbon biological sequestration, in particular the use of technologically adequate photosynthetic strains may be one of the most promising methods for the reduction of the CO_2 emissions in the energy sector, both from the cost and from the environment points of view. Use of accelerated photosynthesis of the selected microalgae strains operate as an intensive natural reducing agent of CO_2 in the flue gas produced by fossil coal power plants and they produce, by cell biosyntheses, lipids, as an alternative primary source for biodiesel and horticulture oils, carbohydrates, proteins, carotenoids and other compounds that can become high added value final products. Thus besides giving environmental and economic benefit, large scale algae cultivation can create a large number of jobs at different levels in the society.

The review presents some of the advantages brought by the microalgal culture in the sustainable CO_2 capture and sequestration from industrial emissions. The combination of the three roles of microalgae – CO_2 fixation, wastewater treatment and biofuel production – has the potential to maximize the impact of microalgal biofuel production systems, and has accordingly been investigated. However, a number of crucial research gaps remain that must be overcome to achieve full-scale operation, including: (i) improved algal growth and nutrient uptake rates; (ii) integration of biosystems with waste gas, wastewater and water reclamation systems; (iii) improved gas transfer and mixing; (iv) improved algal harvesting and dewatering; and (v) lifecycle analysis (LCA) and associated economic assessment. In addition, there is a lack of fundamental information needed to rationally optimize the performance of existing bioreactors. Novel bioreactor configurations and designs are also needed that promote microalgal growth, characterized by volumetric productivities at least one order of magnitude above those of conventional open pond facilities.

Finally, a key challenge for microalgal biodiesel production is the use of microalgal species that can maintain a high growth rate in addition to a high metabolic rate, thus leading to significant lipid yields. This major challenge can be duly addressed via extensive bio-prospecting or target oriented genetic engineering – both of which are now starting to appear as promising approaches.

India as developing economy produces over 170 million metric tons of CO_2 annually; contains abundant saline water; receives abundant sunlight; and has an impressive knowledge base and technical expertise within the energy industry. Thus India has a unique opportunity for algae production because it contains the basic resources needed to grow algae in abundant quantities and also to contribute in the mitigation of climate change.

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