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Review of Microalgae for Intensified CO2 Fixation & Sustainable Bio-Fuel Production

PhD Scholar Manish Sutradhar
College of Environment Hohai University
Nanjing, China
manishsutradhar92@gmail.com

Abstract– Microalgae are the convincing oxygenic photoautotrophic organisms furnished with tremendous potential of performing environmental services and energy recovery to promote carbon neutral bio-economy. There is a major challenge to the global sustainability due to unbalanced production of the CO2. The concentration of CO2 is rising gradually primarily due to human activities such as burning of fossil fuels leads to increase the level of carbon dioxide and has a different ratio of heavy-to-light carbon atoms, so it leaves prominent footprints that instruments can measure. Technologies have thus been developed for enhanced biological carbon fixation. This review briefly examines the current technologies available for enhanced micro algal CO2 fixation and specifically explores eventual production of bio fuels and/or added-value products, with an emphasis on its productivity.

Keywords:- Microalgae, photo-bioreactors, bio-energy, CO2 mitigation.

I. INTRODUCTION

Carbon is essential for all cellular activities, growth and division therefore life on earth is mainly based on organic macromolecules. A number of metabolic reactions involvecarbon dioxide fixation, but they are not necessarily sustaining life. Indeed, many of the actual living organisms fulfil this need by directly utilizing organic molecules that have been synthesized by primary producers. The burning of fossil fuel posses great challenge to world wide sustainability due to increase in atmospheric CO2 [1]. Technologies that are available for CO2 removal/capture include physicochemical absorbents, injection into deep oceans and geological formations, and enhanced biological fixation.

Lithium hydroxide is typically non-renewable form of adsorbent and requires significant space for storage. Other abiotic methods are based on direct injection of CO2 into the deep ocean, geological strata, old coal mines, saline aquifers, oil mines as well as mineral carbonation of CO2. These methods present significant challenges, including high space requirements and potential CO2 leakage over time [2]. Substantive net reductions in CO2 emissions to the atmosphere can be addressed via biological CO2 fixation.

Microalgae have attracted a great deal of attention for addressing CO2 fixation and bio-fuel production because they can convert CO2 (and supplementary nutrients) into biomass via photosynthesis at much higher rates than conventional bio-fuel crops can [3, 4]. The biomass may then be transformed into hydrogen & methane, using processes mediated by anaerobic bacteria [5]. Micro algae mediated CO2fixation and sustainable production of biofuel production can be rendered by coupling microalgal biomass production with existing power generation and wastewater treatment facilities (Figure 1).

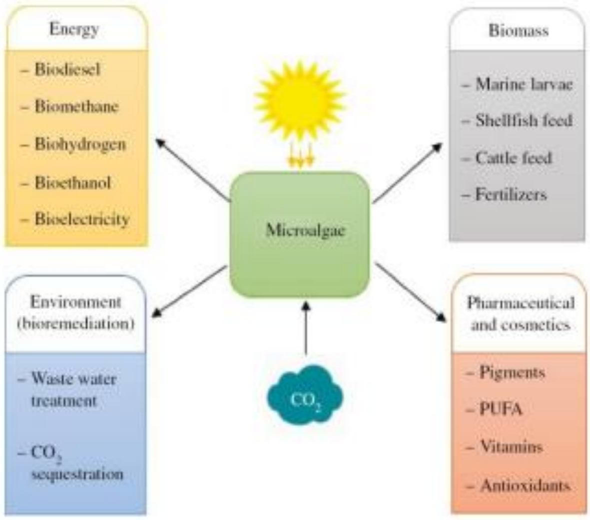

Fig 1. Different applications of micro-algae.

Microalgae can utilize polluted water, such as agricultural runoff or municipal, industrial or agricultural wastewaters, as a source of water for the growth medium as well as a source of nitrogen, phosphorus and micro nutrients [6]. Hence, an additional economic and environmental cost exists as a result of the decreased incentives of water and chemicals required for the formulation of the growth medium, while providing a pathway for wastewater treatment.

II. METABOLIC PATHWAYS UTILIZED BY MICROALGAE

Phototrophic metabolism- Is a process of growth that uses light as a source of energy that is converted into chemical energy through the process of photosynthetic reactions.The carbon source may be supplied on a large scale from an emission point source of a microalgae cultivationsystem, such as power plants, which offers the possibility of recycling exhaust gases i.e. CO2. However, photoautotrophic organisms cultures as require long cultivation periods and result in low cell concentrations, as Chlorella fusca var. vacuolata, Scenedesmus obliquus and Anabaena variabilis. [7,8].

Heterotrophic metabolism: Is aprocess of growth that only uses organic compounds as asource of energy and carbon. Some microalgae genus such as Nitzschia, Chlorella, Scenedesmus & Tetraselmis have the ability to switch between phototrophic and heterotrophic metabolism according to environmental factors & conditions, for example heterotrophic metabolism may be inhibited by the shortage of carbon source [9].

Mixotrophic metabolism: Is a variation of the heterotrophic system, in which CO2 & organic compoundsare assimilated, which enables the operation of photosynthesis and respiration. The mixotrophic growth process can significantly improve biomass productivity (highest growth rate and cell density), reducing production costs by using glycerol and /or glucose as a source of carbon. Mixotrophic profiles have less light dependence and show high production rates as C. pyrenoidosa, S. obliquus and which make this metabolic profile more attractive for a variety of purposes, especially in CO2 mitigation and wastewater treatment technology.

Photoheterotrophic metabolism: Is also known as photoorganotrophic metabolism or photo-assimilation is a metabolic profile in which light is necessary for the use of organic compounds as carbon sources, such as in Platimonas convolutae T. gracilis [10],[11].

III. WASTE WATER AS A SOURCE OF CULTURE MEDIUM FOR MICRO ALGAE GROWTH

Domestic wastewater are suitable for the growth of microalgae as it contains organic carbon, nitrogen, phosphorus and other compounds, as a source of nutrients for their development [12]. Wastewater provides ideal conditions for bacterial growth that helps for the decomposition of organic however, bacteria are less efficient in the removal of inorganic nutrients such as phosphorus, which is usually the main cause of eutrophication of the freshwater ecosystem. Thus, an additional process following bacterial treatment must be applied before it releases into natural waterways, which tends to increase the process cost .Different fractions of raw sewage, urban sewage, and pretreated effluent at different levels have been tested as culture media for microalgae, showing satisfactory results in biomass productivity (Table-1) [13],[14].

Table1. Metabolic profiles and biomass yield of various micro-algae under different cultivate medium [13]-[17].

Species	Wastewater cultivated medium	Metabolic pathway	Biomass yield (gm/l/day)
Chlorella pyrenoidosa	Diluted primary piggery	Mixotrophic	0.3
Chlorella vulgaris	Municipal wastewater	Mixotrophic	0.251
Phormidium autumnale	Slaughter house wastewater	Heterotrophic	630
(Phormidium Sp)	Chemical Industry	Phototrophic	122-140
Chlorella pyrenoidosa	Landfills lechate	Photo hetrotrophic	9

Treated effluent contains nutrients (nitrogen and phosphorus) and trace elements (K, Ca, Mg, Cu , Fe, and Mn) that are essential for metabolism and the growth of microalgae . Its cultivation using wastewater is influenced by various factors. The efficiency of growth of these organisms is dependent on the control of critical variables, including temperature, availability of light, pH, CO2, O2, and especially nutrient concentrations [15].

The presence of mercury (Hg), cadmium (Cd) & other toxic organic compounds and contaminants such as bacterial pathogens and predators (zooplankton) results in inhibitory effects on microalgae growth. The presence of suspended solids and turbidity, especially in urban wastewater, can affect the penetration of light, which is a critical factor for microalgae growth. In heterotrophic or mixotrophic cultivations, this light limitation can be overcome through the consumption of high levels of total organic carbon (TOC) in the form of acetic, propionic, ethanol and butyric acids. In certain cases, however, it becomes necessary to supply additional sources of organic carbon to the culture, generating additional production costs. Researchers have investigated cultivation techniques using wastewater as culture medium with an interest in reducing the cost [16].

IV. DIFFERENT TECHNIQUES OF MICROALGAL CULTIVATION

Microalgae cultivation systems are of two types i.e. open and closed. Open ponds in lane format and turf scrubbers are most popular of these systems. Closed systems, also known as photo bioreactors, have higher diversity of configuration & shapes. The most common being bubble column, tubular, airlift & flat panel [18]. Open ponds are one of the oldest and simplest systems for microalgae production [19]. Generally, these systems consist of an impermeable oval pond with a continuous or divided form containing a series of plates where water is circulated and transferred through tanks to achieve uniform mixing of nutrients and proper algae growth [18]. Open systems do not effectively use the provided CO2, which easily escapes from the culture medium due to the shallow depths of the system and poor efficiency in the mass transfer of CO2 and its fixation in these systems ranges from 10 to 30%.

The main advantage of open ponds is their simplicity, resulting in very low operating costs. However, there is a higher chance of contamination by other microorganisms, including bacteria and other seaweeds, and losses by evaporation or diffusion of CO2 into the atmosphere [18]. Additionally, there is a requirement for large land areas and difficulty in controlling environmental variables that may interfere with the cultivation process, such as temperature, luminosity and rainfall [20]. Raceway ponds and similar systems differ from open ponds by having paddle impellers i.e. artificial mechanisms of agitation [21]. In a study performed by Wu et al. [22] on the cultivation of Scenedesmus sp. LX1 in a 0.20 m deep open pond fed with secondary wastewater, the maximum rate of biomass production achieved was 20 gm-2d -1 .A new technology for treating wastewater called Turf Scrubber uses clusters of several filamentous algae species seems to be effective in improving the quality of agricultural wastewater and domestic and industrial sewage. This system consists of diverse group of algae that grow attached to a screen or a support coupled to a chute through which polluted water flows, providing treatment through the uptake of organic and/or inorganic compounds during photosynthesis [23].

According to Mulbry et al**.,[**24] this technology has been shown to provide potential nutrient treatment for manure effluents and agricultural runoffs while also yielding biomass suitable for harvesting and use as feedstock for biofuel production. Photo bioreactors are designed to produce strains of photosynthetic microorganisms rich in high-value products, with the advantage of metabolic flexibility of microalgae; by properly adjusting the culture condition the generation rate of the desired product can be improved [25].

According to the physiological characteristics and specific growth factors of algae, closed photo bioreactor must be designs [26]. In contrast to open cultivation systems, photo bioreactors allow microalgae monoculture by controlling the contamination while enabling the control of variables such as pH, temperature, CO2 and concentration light. These systems result in smaller losses of CO2 and water by evaporation, have high rates of CO2 mass transfer and allow the production of high quality bioproducts [27]. Molinuevo Salces et al.[28] utilized two configurations of photo bioreactors, an open-type photo bioreactor open to the atmosphere and a tubular type photo bioreactor closed to the atmosphere, to compare the treatment efficiency while using degraded swine slurry as cultivation medium.

The most significantly results of removal were for ammonium, in which the recovery by biomass assimilation in the open configuration ranged from 38–47%, whereas the closed type achieved a value 31% through nitrification– denitrification, and approximately 80% phosphate removal was achieved regardless of the configuration and biomass P content, which was slightly higher in the closed type reactor. Different types of photo bioreactors have been developed, and they can be classified according to their reactor geometry: tubular, vertical column and flat panel. Tubular photo bioreactor systems typically composed of a series of transparent tubes exposed to solar radiation and built in different patterns (e.g., straight, curved or spiral) with a relatively small diameter (generally less than 0.1 m) to ensure the high productivity of biomass[29].

A gas exchange system through which air, CO2and nutrients are added and O2 is removed is coupled to the main reactor. Culture medium is circulated from a reservoir with a mechanical pump that maintains the bioreactor in a highly turbulent flow, providing total mixing and preventing deposition of biomass. Tubular photo bioreactor systems that circulate the culture through an airlift device is especially attractive for many reasons: circulation is achieved without moving parts, providing a robust culture and a reduced potential for contamination; cellular damage associated with mechanical pumping is avoided; and the airlift device combines the function of a pump and a gas exchanger for removing the oxygen produced by photosynthesis [30]. Vertical-column photo bioreactors are usually cylindrical, with a ratio of up to 0.2 m and a 4 m height. The height restriction is associated with gas transfer limitations and the resistance of the transparent material used to build the columns. Bubble column photo bioreactors are cylindrical containers with heights more than twice their diameter [31]. Biomass separation: In the production process the critical step is the separation and recovery of microalgae biomass from the growth, accounting for approximately 20–30% of total costs [32].

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Micro algal cells size vary from 5 to 50 mm, form stable suspensions in culture media due to their negative surface charges, and secrete organic compounds that maintain their stability in the dispersed condition [33]. The choice of separation technique depends on the properties of the specific microalgae, including density, size and value of the desired products. Micro algal cultures are usually very dilute suspensions, with concentrations below 1 g/l. They can be ideal for light penetration and can provide the necessary biomass for production processes of bio-products of interest; a minimum concentration of 15% (wv-1) of microalgae is required for lipid extraction and bio-fuel production, [33]. To remove water and large volumes of algal biomass, an appropriate harvesting method may require one or more steps involving physicochemical or biological processes to achieve the desired solid-liquid separation. Experience has shown that a universal harvest method for all species of microalgae does not exist, although this is still an active research area.

Techniques currently used in micro algal harvesting include centrifugation, flocculation, sedimentation, filtration and electro coagulation [32].

1. Coagulation/ Flocculation: Flocculation is the process in which coalescence of suspended algae cells weakly joined large conglomerates. Initially, the suspended cells aggregate into larger particles through the interaction between a coagulating agent and the surface charge of the cells. Subsequently, the aggregates coalesce into large flakes, separating from the suspension called flocculation. The flocculation technique is considered an effective method for quickly processing large amounts of biomass [31].Various chemicals have been tested as flocculating agents, including a variety of inorganic salts of polyvalent metals and organic polymers called poly- electrolytes. More recently, microorganisms have been applied to the flocculation of certain microalgae species. Operations involving physical processes, such as sedimentation, flotation, centrifugation or filtration, usually require a preliminary stage of flocculation as a manner of grouping the cells. The use of inorganic coagulants produces a large volume of sludge, causing micro algal death or inhibition of growth [33].

Although aluminum is an effective coagulant for some microalgae species, the use of metal salts may be unacceptable when the biomass will be used in aquaculture or as animal feed or fertilizer. Ideally, flocculants should be low cost, non-toxic and effective at low concentrations.[34] Commonly used salts include ferric sulfate (Fe2 (SO4)3), ferric chloride (FeCl3) & aluminum sulfate (Al2(SO4)3) [35]. Udom et al.[36] compared different coagulants - metal salts (aluminum, ferric chloride), cationic polymers (Zetag 8819), anionic polymers (E-38) and natural sources (Moringa oleifera and Opuntia ficus indica) at different dosages to study their efficacy at separating suspensions of microalgae grown under a semi-continuous system using sludge from the anaerobic digestion of municipal sewage. The best results were observed for metallic aluminum salts, ferric chloride and cationic polymer, all of which reached recovery efficiencies of greater than 91%.

2. Electro-Chemical Methods- It involves physicochemical processes that use electrical currents to dissolve sacrificial metal electrodes to provide the necessary ions for coagulation/flocculation. In contrast to chemical flocculation, electrochemical methods do not introduce anions that would result in the reduction of pH [35]. Electro-coagulation and electro-flocculation have been successfully used as alternative methods for producing metal hydroxides for the separation of micro algal biomass.Technologies combining electro-coagulation and electro-flotation have attracted considerable attention for the separation of algal biomass. In these processes, metal ions released by the anode through electrolytic oxidation attack the cells in suspension, promoting their coagulation. At the same time, micro- bubbles of oxygen and hydrogen generated at the anode and cathode, respectively, promote adhesion to form larger flakes, which may be removed by cultivation techniques and phycoremediation process of the wastewater.[36] Uduman et al.[37] observed a recovery of more than 98% of two marine micro algal species (Chlorococcum sp. and Tetraselmis sp.) using electro-coagulation.

3. Filtration: The most competitive method of harvesting is the filtration, and it is possible to concentrate microalgae with efficiencies ranging from 10 to 20% (ww1),although the process requires relevant maintenance, including the cleaning and replacement of filters [38]. Available filtration techniques include microfiltration, ultra filtration, pressure filtration & vacuum filtration. Pressure or vacuum filters can be used to concentrate microalgae strains with large cell dimensions, such as S. plantensis. The recovery of algae such as Chlorella and Dunaliella, with cell dimensions similar to those of bacteria, cannot be carried out by methods involving vaccum filtration or pressure [39].

4. Centrifugation: Most microalgae may be recovered from a dilute suspension through the application of centrifugal force. Centrifugation is a dewatering method for concentrated biomass that has higher life cycle energy consumption (700 MJ/ dry tone of algae), GHG emission (50 kg CO2 eq. /dry tone of algae) and equipment cost than other methods [37-38]. However, it may still be considered a viable alternative, especially in the production of microalgae to obtain high-value products or when used in an integrated manner together with other preliminary harvesting techniques [39]. Energy-efficient methods must be developed to allow the application of this technique in microalgae cultivation prior to centrifugation [40].

5. Flocculation By Increasing Ph- Flocculation often occurs spontaneously in micro algal cultures when the pH is in alkaline condition usually above 9. This technique is generally known as auto-flocculation because it occurs spontaneously upon to photosynthetic CO2 depletion. Auto-flocculation is associated with the formation of calcium or magnesium precipitates, and most water contains magnesium concentrations sufficiently high for this process to occur. Under certain conditions, these precipitates carry a positive surface charge that can drive flocculation through charge neutralization.

Flocculation at high pH is caused by the formation of inorganic precipitates, resulting in high mineral concentrations in the flocculated biomass [41]. Increasing the pH can also influence the load of micro algal cells and modify existing forms of metal ions in suspension due to its hydrolysis. Thus, flocculation induced by pH increase is an attractive alternative to reduce costs and power consumption, and it is non-toxic to algae cells and eliminates flocculant utilization. Another advantage of this method is the potential for recycling the growth medium, as the flocculated microalgae are completely removed.[36] Among micro algal species that have auto-flocculant in properties are Ettlia texensis, Ankistrodesmus falcatus,T. suecica & S. obliquus [42].

6. Major Products- Products that result from microalgal cultivation include animal and human food products and fertilizers, as well as industrial chemicals and bio-energy feedstock. The use of micro algal biomass is in fact a fastgrowing market as healthy human food, or as an ingredient in the formulation of animal and aquaculture feed [43]. Presently, micro algal biomass is an essential source of nutrients in aquaculture [43], owing mainly to its high content of polyunsaturated fatty acids, which are wellestablished growth factors. It has also been used as a functional food in the form of tablets or powder, and as nutraceutical food additives [44]. Microalgae are used worldwide as agricultural fertilizers, which, besides their significant nutritional content, can improve the waterbinding capacity and the mineral composition of the soil.

V. CHALLENGES & RESEARCH NEEDS

Enhanced biological fixation of CO2 has attracted a great deal of attention because it leads to production of bio fuels or other industrial products with a market value, together with a potential reduction in greenhouse gases (GHGs) and treatment of impaired waters. In addition, the high growth and CO2-fixation rates of microalgae lead to a number of advantages as compared with conventional energy oil crops (e.g. palm oil), especially because the yields of oils, on a mass basis, are considerably higher. Finally, micro algal biomass can be used for animal and human food formulation or as land fertilizer. However, several challenges for micro algal based CO2 sequestration remain, some of which were addressed in this review and are further summarized below. Most studies reported to date have been performed on the bench-scale, and were conducted under strictly controlled conditions. As a result, little is known about the feasibility of reactor scale-up, or the effects of competition. by other microbial species inadvertently introduced into the bioreactor with the feed stream.

Current investigations focus mainly on closed bioreactors, whereas future research should also consider open systems, owing to the possibility of more widespread use of biological CO2 mitigation. Among these, technologies that support the supply of adequate amounts of CO2, nutrients and light to micro algal cells, consume minimal energy, and release less CO2 into the atmosphere are in special demand. Enhanced levels (typically well above its atmospheric level) are needed for efficient micro algal growth and metabolism, and currently are major contributors to the overall cost of micro algal cultivation.

However, different sources of CO2 and supplementary nutrients will greatly improve the overall environmental performance of micro algal based bio-energy production. Future research should explore existing sources, such as CO2 from ammonia plants or flue gases from power stations. Furthermore, nutrients could easily be extracted from wastewater or agricultural wastes owing to their richness in nitrogen and phosphorus. Note, however, that the quality of the flue gas might hamper specific applications in the medical and food fields. Studies might also be required to discern whether micro algal biomass production using wastewater produces sufficient-quality effluent for discharge into the environment, or even eventual reuse.Waste streams are, in general, small compared with energy demands; as a result, transportation costs to concentrated production sites should be assessed in advance. Co-digestion of microalgae with wastewater sludge for biogas production should also be considered, because this strategy could be integrated into the existing wastewater infrastructure.

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