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Sustainable Sequestration Of Carbon Dioxide – A Review

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Abstract

Among various GHG gases causing global warming, the contribution by CO_2 alone is about 60%. Post combustion carbon capture is most viable technique compared to pre-combustion and oxy-fuel combustion CO_2 capture techniques used for conventional coal based thermal power plants. Cryogenic separation, chemical absorption, adsorption, membrane based separation etc. belong to post combustion carbon sequestration technology however these methods have some or other disadvantages. Ocean injection results in lowering of pH of sea water thus affecting bacteria zooplankton and benthos species. Moreover following a considerable period of time, the stored CO_2 can leak. Controlled addition of CO_2 in ready-mix concrete, as produced in the United States, Canada and Singapore improves the compressive strength without sacrificing performance or durability. Microalgae consumes substantial quantity of carbon dioxide (1 Kg dry algae biomass consumes about 1.83 Kg CO_2) and hence very effective in bio-fixation of CO_2 waste as well as in improvement of air quality. Accumulation of oil (about 20 to 50% weight of dry biomass) and fast growth of microalgae make microalgae cultivation a commercially interesting and promising technology to mitigate global warming problem and generation of bio-fuel alongwith other benefits namely production of nutrient dense foods, chemicals and fertilizer.

Keywords: Greenhouse gases; ready-mix concrete, sustainable; microalgae; biomass; bio-fixation

Introduction

Still now, thermal power plants mostly are fulfilling the rising energy demand and thus constitute major cause of CO_2 emission. Rapid industrialization including installation and commissioning of various chemical manufacturing plants, urbanization, deforestation and increased automobile exhaust emission constitute increasing release of carbon dioxide. Due to these human activities,CO_2 concentration in atmosphere has risen upto 380 ppm from 280 ppm (parts per million) with a span of last50 years [1]. Due to this, various detrimental effects such as rise in sea level, melting of floating iceberg, and global warming warn the subsistence and growth of humankind. Hence it is utmost important to design suitable methodologies to efficiently collect CO_2 and transform into industrially suitable materials.

From the flue gas CO_2 is to be removed and then it is required to be stored for subsequent use and thus the negative impacts of carbon dioxide release could be reversed. The concept of circular carbon economy (CCE) deals with various technologies associated to capture carbon at emission site and store for subsequent use for manufacture of fire extinguishers, plastic components, fuels, fertilizers, soda ash, food and drinks, building materials etc.[2]. The paper has been undertaken to discuss different latest methods required to be adapted for controlling and solving the critical issue of

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global warming arising due to increased concentration of CO_2 in the environment.

Various approaches of Carbon-Di-oxide sequestration:

Till date the Carbon Capturing and Storage (CCS) has been viewed as the most favorable option for CO_2 sequestration directly from emissions, the large stationary sources [3]. CO_2 can be captured directly from its source of formation before polluting the atmosphere [4,5]. For the storage, the confined CO_2 can be compressed, transferred, and injected within underground reserve area [6,7]. The captured CO_2 can be recycled by different industries like cement, oil, food processing, power plants, iron & steel industries [8]. For the transportation of CO_2 over a long distance, the structure and pipelines are to be properly configured. It must be configured in proper dimension to hold out against the velocity and pressure of the fluid. The USA confirms the CO_2 transportation around 50 to 60 million tons/year over long distances [4]. In the indirect method of carbon capturing, CO_2 can be trapped by plants during photosynthesis. This process is not only environment-friendly also capable of trapping CO_2 into the soil [9].

Carbon capturing approaches:

There are three major processes for Carbon capturing namely post-combustion, pre-combustion and oxy-fuel combustion [10].

Several capturing techniques such as absorption, adsorption, biological technique, extraction ,membrane technology as well as hybrid technique have been explored to address the ever-growing Global warming issue [11,12].

Although absorption is considered as the most common, it is highly energy demanding. Additionally, the used solvent may be corrosive for the vessel depending on its nature. Currently Membrane-based CO_2 separation becomes a promising alternative for traditional chemical absorption technology.

In this review, techniques like short term injection, utilization of carbon dioxide in ready-mix concrete, absorption, membrane technology have been discussed. Various advanced techniques based on different advanced materials such as ionic liquids, porous organic polymers, zeolites, metal-organic frameworks and covalent organic frameworks also have been discussed. Sequestration of CO_2 using photosynthetic reactions, one of the best ways for sustainability, also has been reviewed in detail.

Short-term sequestration:

Carbon-dioxide can be injected directly into sinks instantaneously. But most sinks leak the sequestered CO_2 in the remote future. However, CCUS in geothermal storage is very important due to relative increment of CO_2 emission and highly attractive alternative in geothermal power generation [14].

Ocean Injection:

Though ocean injection can bring down global warming issue instantaneously but that can leak the sequestered CO_2 in distant future. Moreover, this way of sequestration would result in lowering of pH of sea water thus affecting the species like bacteria; zooplankton; and benthos [15]. To resolve the issue, the delocalized CO_2 can be used for ocean fertilization. In this case the photosynthetic organisms absorb CO_2 during photosynthesis; their growth accelerated with nutrients and dead organisms enrich ocean fertility by remineralization. On the contrary, the marine ecosystem is affected by alteration in phytoplankton structure. Moreover, anaerobic decomposition under ocean may liberate methane, nitrogen monoxide and create disadvantages of greenhouse gases again [16].

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Geologic injection:

Geologic injection refers Mineral carbonation; coal seams; and Enhanced oil recovery (EOR).

Mineral carbonation: -In this process, silicates are converted into carbonates with following reaction [15].

$$(Ca, Mg)_xSi_yO_{x+2y} + xCO_2 \rightarrow x(Ca, Mg)CO_3 + ySiO_2$$

This is a long-term natural process that occurs by chemical weathering. The rate of reaction may be accelerated with the solubilization of mineral ions in strong acids or running under high pressure of CO_2. But discharge of strong acids harms the system and surroundings, and high pressure will increase operating cost [16,17]. The mechano-chemical process was also studied. In these method, various forms of natural silicates were ground repeatedly to absorb gaseous CO_2. But the carbon fixation yield was not significant compared to energy requirement for grinding action [18]. The surface activation [19] and involvement of biological catalyst [20] also investigated to enhance rate of reaction. However mineral carbonation technology has not much scope as it impacts mineral industries for a huge requirement of metal oxides [16].

Coal seams: - This case permanent CO_2 retention is possible with replacement of methane gas present in porous coal beds. If methane replacement is done by absorbing CO_2, the permanent retention of carbon is possible [21]. This methane recovery process is highly efficient along with CO_2 sequestration [22].

EOR: - In this process the oil movement and its extraction in reservoirs are enforced by captured CO_2. The CO_2 can again be recycled for reuse. However, the process is economically not viable for huge energy requirement to remove CO_2. To resolve the issue a plant for CO_2 recovery can be combined with enhanced oil recovery to decrease the conveyance expenses. In spite of that this remains too costly [15].

Pre, post & Oxy-fuel combustion:

In Pre-Combustion technique, syngas (a mixture of H_2 and CO) is derived from fossil fuel by partial oxidation or gasification. The reaction is preceded by water gas formation by steam pursued by water-gas shift reaction before the actual combustion takes place [23]. Carbon dioxide gas is separated from the synthesis gas using physical/chemical absorption process generating H_2 concentrated stream. This H_2 may be reused as a gaseous fuel and utilized for power generation. Thus CO_2 emission can be eliminated in pre-combustion with consecutive steps [24, 25]. The pre-combustion becomes easy at higher concentrations & pressure and decrease energy requirement about10% to 16% [3]. As for example during ammonia processing, both hydrogen and carbon dioxide gases are produced but CO_2 is removed prior to synthesis ammonia synthesis [26].

But commercial application is the major barrier for gasification in pre-combustion technique. Although CO_2 concentration is high in pre-combustion, but the cost of equipment is higher and extensive supporting systems are required [27].Additionally, the pre-combustion gas stream containing CO and CH_4 create great concern having toxic effect of CO and greenhouse effect of CH_4. Moreover, the existence of H_2S even in trace amounts creates a serious hazard especially for the stability of metal-organic frameworks if it is used to separate CO_2 [24, 28]. Overall the pre-combustion technique is not a good option for high cost, low efficiency and high-temperature demands [29].

Oxy-combustion CO_2 capturing process is one of the effective ways for CO_2 elimination [30]. In this process combustion takes place with

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nearly pure oxygen instead air [10]. In consequence the flue gas contains mainly water vapour & concentrated CO_2. The CO_2 purification obtained easily by condensation of water vapors [3]. This process can integrate the pre-combustion and the post-combustion both in case of fuel gasification taking place almost pure oxygen environment [28]. But oxy-combustion is not cost effective for the requirement of large amount of cryogenic O_2 production. This method may be practiced to newly build or reconstructed plants [27].

In Post-combustion, after complete combustion carbon dioxide gas is captured from the flue gas and before it pollutes the atmosphere [31]. This is Retrofit technology option [27].

In comparison the oxy-fuel combustion is associated with newly constructed power plants while for gasification units the pre-combustion capture is more suitable [32]. However, in traditional power plants, the direct combustion occurs. So being an “end-of-pipe” technology, post-combustion is most recommended among all [33]. Figure 1 represents the CO_2 capture schemes.

Technical approach:

Chemical absorption:

Among various post-combustion techniques referred above, the most acceptable and feasible for implementation is the chemical absorption [34]. Chemical absorption can be combined with various solvents (amines [33–36], nanofluids [37, 38], ionic liquids [41–43], amino acid salt solutions [44, 45], etc. Monoethanolamine (MEA) is most acceptable among different amines [46].

Currently, various companies are implementing larger-scale power plants by chemical absorption process in collaboration with research organizations. As for example the first post-combustion capture pilot plant with CO_2-scrubbing plant contracted in July, 2009 at Niederaussem in Germany [47]; CO_2 capture plant of Dong power plant situated in Denmark [48] are mentionable. The first and largest commercial CCS project is SaskPower’s Boundary dam, integrated with Carbon Capture and storage [49] and by July, 2016 it captured about 1 million ton CO_2 successfully.

Although the absorption (chemical) process is an established technology but is not cost effective as it is energy intensive. Optimization can be done by modification of parameters, process and solvents [50].

Membrane technology:

To remove CO_2 from a gas stream using membrane separation, the part of CO_2 permeates across the membrane known as permeate and the residual flue gas has been known as retentate. After certain time, the permeate sideCO_2 concentration becomes higher. The compressor & vacuum pump need to be used to enhance the pressure gradient among feed side & permeate side so as to maintain the required driving force for membrane separation [51,52].

The degree of separation is influenced by selectivity & permeability of membrane. It depends on membrane materials and module. Among various membrane materials such as organic (polymeric), inorganic (e.g. ceramic), and combined (mixture of organic & inorganic) membranes are commonly used. Among various configuration of membrane module, spiral wound [53, 54], hollow fiber [55],& envelope [56] are primarily accepted.

As per research findings, membrane technology has no added advantage over Chemical absorption process [6], but in combination of these two processes can optimize the cost and energy requirement [14].

Use of CO_2 in ready-mix concrete:

Use ofcapturedCO_2in concrete, has been practiced by producers of ready-mix concrete (RMC) in Canada the USA and Singapore. The Concrete is widely used and has been the most

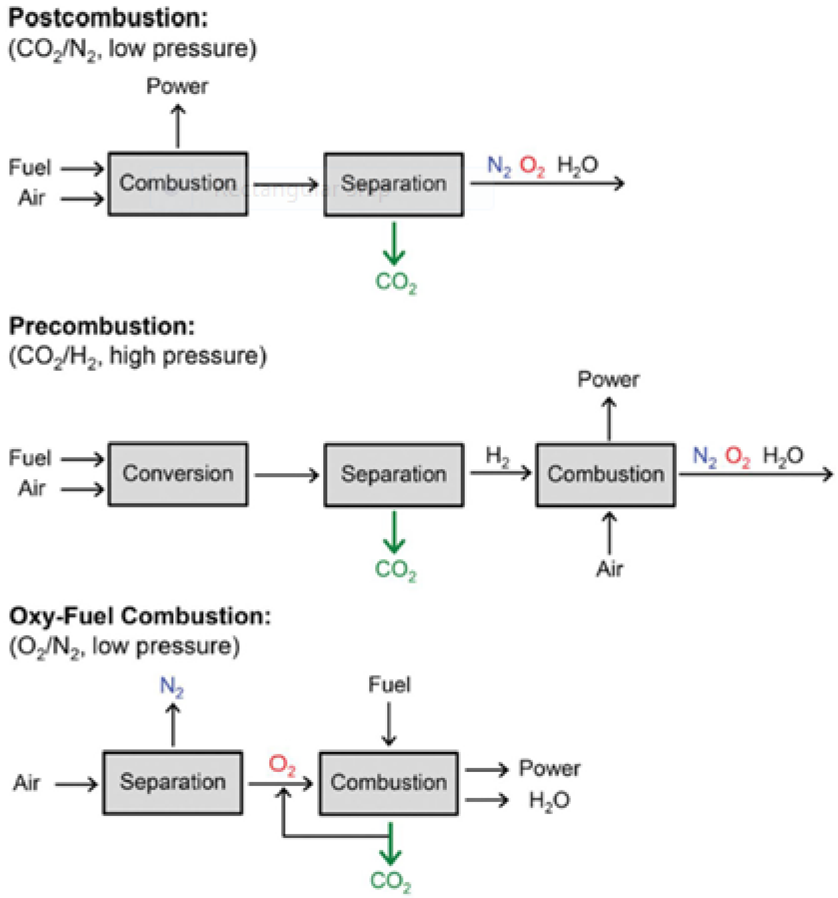

Fig.1. Basic Schemes of different CO_2 Capture Processes **[1].**

important construction material. According to requirement, RMC is manufactured batch wise and subsequently, used at the particular site. Compared to various other materials, concrete is less energy intensive and has lower carbon footprint. Portland cement that is used to produce concrete emits large quantities of CO_2. During cement production, limestone ($CaCO_3$) is converted to reactive calcium silicate wherein CO_2 is a by-product [57,58]. It has been reported that manufacturing of cement is accountable for 8% of planet warming CO_2release which is substantially higher than global carbon release from aviation [59].

According to the International Energy Agency, for cement industry, it has been aimed to reduce CO_2 emission to 1.55 gigatonne in the 2050 [60], while during the same time cement production has been anticipated to enhance by about 50%. To implement the said target of reducing CO_2 emissions, few approaches were decided to be followed. Reduction of CO_2 emission through enhanced use of alternative and suitable raw materials, taking measures so as to enhance the energy efficiency of cement kilns and capturing of carbon dioxide released from such plants are the required approaches.

Researchers have studied the impact of injection of carbon dioxide in batching and mixing. It is reported [60] that the idea of CO_2 utilization can create lower carbon concrete products. The injection of CO_2 was found to improve of the concrete in terms of compressive strength. Sean Monkman and Mark McDonald [61] have studied the outcome of the injection of CO_2 during batching after concrete was produced. Using a metering device, the flow of pressurized liquid $CO_2$was controlled into the concrete via a discharge conduit during batching. The liquid, upon reaching the atmosphere, after getting discharged undergoes phase transition with the formation of CO_2 snow which is fine particles of solid carbon dioxide and CO_2 gas. During investigation, controlled supply of carbon dioxide was made to flow intermittently into freshly prepared concrete for a particular duration. CO_2, upon mixing with fresh, wet cement, react with calcium ions to form calcium carbonate and thus gets solidified and bound chemically with the concrete. The fresh concrete thus produced was undergone standard tests such as ASTM C231 which is a standardized test method to determine for Air Content of fresh concrete, ASTM C143, which is a standardized test method for Slump of hydraulic-cement Concrete. Furthermore, another test, ASTM C39 was also carried for evaluating compressive strength of hardened concrete cylinders. Investigation showed that addition of CO_2 could bring improvement of compressive strength of concrete.

Quantification of direct absorption in concrete is a difficult task. Generally carbon dioxide applied in concrete consisted of 50% solid and 50% gas. The combined overall efficiency is estimated as approx. 60%. So though the dosage in the study has been specified as 482 gm / m^3 of concrete, actually 289 g ofCO_2 was actually fixed. Therefore an estimated 14.4 tonnes of CO_2 was actually absorbed over $50x10^3$ m^3 of concrete produced. In terms of compressive strength, a drop of about 11-13% was observed in air entrained reduced binder batches. However addition of CO_2 was found to enhance the reduced binder concrete strength, the increase was evaluated to 10% at seventh day and approx. 13% at twenty eighth day. Following CO_2 addition, the strength of this reduced binder batch, was found to be almost equal to the strength obtained from the standard mix [61].

Sequestration of CO_2 UsingMOF (Metal organic Framework): These pertain to a class of polymer having permanent porosity. In these materials, coordination of metal ions/clusters to organic ligands to form one, two, or three-dimensional structure occur.

In MOFs, crystalline porous frameworks are obtained due to joining of polynuclear metal clusters by organic linkers. Two dimensional structure of MOFs such as sheets, plates, rings, membranes disc, flakes, walls etc. having large surface area and increased surface / volume value. MOF of erenormous structural diversities and possibilities for design of materials with customized characteristics. Owing to the characteristics of high pore volume, specific surface area, ability to be functionalized and stability render MOFs these good candidates for gas separation. The formation of a MOF has been shown pictorially in Fig.2 [62,63].

One of the deeply researched area is the cyclo-addition of carbon dioxide with epoxides in MOF-catalyzed CO_2 conversion reactions [64]. MOF composites formed by combining MOFs along with other materials, found to be suitable for sequestration of CO_2. Recently MOF-based materials are efficiently utilized for transforming CO_2 into different products using methods such as electrocatalytic reduction, photocatalytic reduction, hydrogenation etc.[64].

Recently emerged electro-chemical reduction reaction of carbon dioxide has become a promising technology which uses green energy to manufacture fuels and valuable chemicals including ethylene, carbon monoxide, methanol, ethanol, formic acid, oxalic acid etc. from CO_2.

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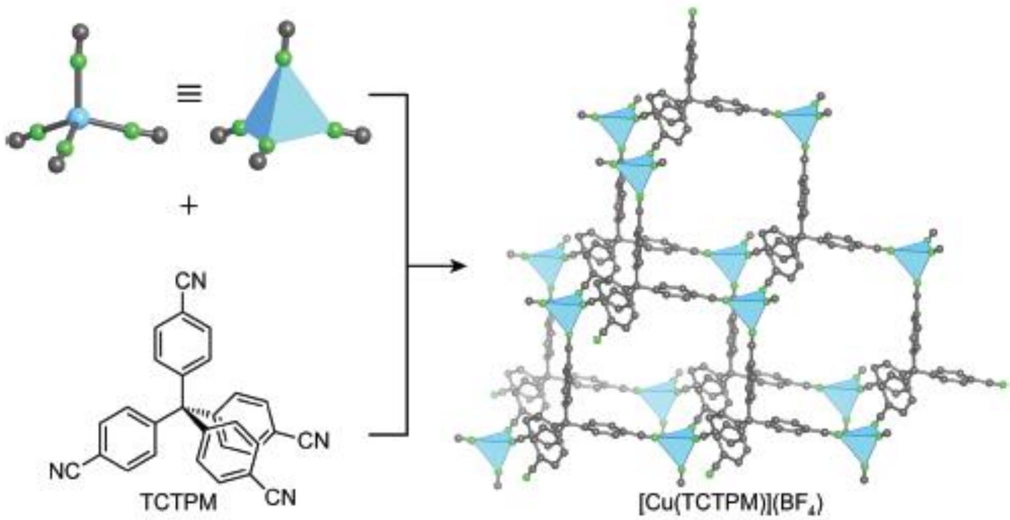

Fig.2.Cationic coordination network crystal structure [Cu(TCTPM)](BF_4)]

(TCTPM =tetracyanotetraphenylmethane].[63].

Recent researches have shown that multicarbon products can be formed from CO_2 using Cu and Cu based modified nanoparticles. In the field of catalysis, copper based metal-organic frameworks have been achieving increasing importance among various other copper-based nanoparticles, due to their electrical, topological their textural properties[65].

Removal of CO_2 using Ionic Liquids:

To overcome various disadvantages of aqueous amine used for scavenging CO_2 owing to several disadvantages of using costly, corrosive amine such as high volatility, considerable energy utilization, the need for choiceof a new solvent had become primarily important [66]. The non-volatility, structure-turnability, relative non-flammability, recyclability, designability and high carbon dioxide absorbing capacity make ionic liquids one of the most suitable materials for capturing carbon dioxide, that can be subsequently transformed into valuable, fine chemicals. ILs are actually salts having lower melting points (less than 100^0C). These consist of cations such as pyrrolidinium, pyridinium, imidazolium, amine etc. and anions such as azolate, carboxylate, thionate, thionate, halide, hexafluorophosphateetc. [67,68]. ILs can be tailor made to achieve optimum CO_2 solubility.

High viscosity of ILs is one of the major disadvantages of using these as scrubbing agent, however viscosity can be reduced by adopting suitable mean. ILs, having both the properties of catalyst as well as solvent, can be utilized in the transformation of carbon dioxide molecules to different organic compounds including formic acid/formats, methanol, carbon mono-oxides etc.[69].

During the last decade, Rosen *et.al.*[70] had investigated the ability of Room Temperature Ionic liquid (RTIL) in the electrochemical conversion of carbon dioxide to carbon. An electrochemical conversion of CO_2 to CO in

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18% aqueous 1-ethyl-3-methylimidazolium tetrafluoroborate was achieved.

Photosynthetic sequestration of carbon dioxide:

0.05% of annual absorption of more than 3800 zetta joules solar energy by Earth, is utilized in photosynthesis by plants to produce biomass [71].Generation of renewable energy instead of full dependence on conventional energy obtained from fossil fuels have been explored in recent years. Generation of biofuel from biomass obtained using photosynthesis not only lowers atmospheric CO_2 levels as a result of photosynthetic reactions, also creates far lower emission than burning fossil fuels. Though the first generation fuel ethanol, produced from starch/ sugar-based crop, has shown the possibility of manufacturing liquid fuels from renewable sources, but had the disadvantages of low energy-conversion efficiency, almost halved energy density compared to oil-based fuels and increased cost. Moreover during conversion of biomass to ethanol by fermentation, considerable CO_2 is also emitted in environment. Moreover first generation biofuels are obtained directly from crops namely cane, sugar b eet etc. cultivated in agricultural field, hence to make the production of biofuel more sustainable, the second generation biofuels are obtained from non-edible plants and thus are not in direct competition with food production.

Various techniques of biofuel production as well as carbon dioxide sequestration from micro / macro algae have been investigated by researchers across the globe. Algal biofuel, obtained through various conversion processes from the oil-rich algae are third generation advanced renewable fuels. Algae can be multicellular (macro algae) or unicellular(micro algae), exists in 3000 breeds. Increased efficiency related to fermentation/ hydrolysis is achieved in case of algae due to lesser content of hemicelluloses and the absence of lignin [72]. A particular type of algae, microalgae is capable of fixing CO_2 in presence of solar light ten times more compared to terrestrial plants [73]. From algal biomass various types of fuel can be obtained using different routes such as biodiesel through transesterification, biogas following anaerobic digestion, bioethanol through fermentation, bio-oil, bio-char and biogas through pyrolysis, also energy can be obtained from direct combustion of algae.

Other uses of algae include feedstock for aquaculture, pharmaceuticals, cosmetics, chemicals, biofertilizers, systhetic substitutes ,hydrocolloids etc. Strict regulation for food safety only permits some health and food products based on *Dunaliella*, *Chlorella*, *Spirulina* species for human consumption [74].

Different groups of algae such as *Chlorophyta*, *Rhodophyta* and *Phaeophyta* are found in a natural habitats such as deep oceans, in rocky shores as well as in freshwater too. Rapid growth potential of microalgae, its high oil content upto 50% dry weight of biomass as well as high CO_2 biofixation (about 1.83 Kg CO_2 per Kg biomass of microalgae) - altogether make microalgae cultivation very beneficial commercially as well as in terms of improvement of air quality and balancing CO_2 level in environment. [75,76,77]. Furthermore, effluent from agro-food industry, if utilized for cultivation of microalgae as a growth medium, will be very much beneficial as it can provide the useful nutrients to algae as well as pave a way to solve effluent discharge problems.[78].

In the past, algae cultivation was be carried out in open ponds- natural or artificial. Shallow and stagnant ponds favor algal growth due to more penetration of sunlight and warm water. However for large-scale production of algae, U shaped raceway ponds with circulation facility are used.

[75].

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Natural cultivation and artificial cultivation (using photobioreactor) of algae has been depicted in Fig.3[79]. For obtaining high productivity of algae in a controlled as well as closed environment, photobioreactor (PBRs) are fed with all growth requirements of algae. Proper control of various parameters namely optimum temperature & pH, culture density, required light exposure, supply of CO_2 and water, mixing type is possible in PBRs.

Bitog et. al in 2011 performed a study on CO_2biofixation taking two species of green algae namely *chlorella vulgaris* and *Nannochloropsis Graditana* in a a tubular reactor at 25^0C temperature with two different initial CO_2 concentrations of 4 and 8 vol% respectively using simulated light enhanced photosynthesis. A greater CO_2 uptake rate of more than 1.70 gm./(lit.day) was found in case of *N. Graditana* at 8 vol% CO_2 concentrations. A cell concentration of $1.7x10^7$ cells / ml was reported on the 10^{th} day of cultivation [79].

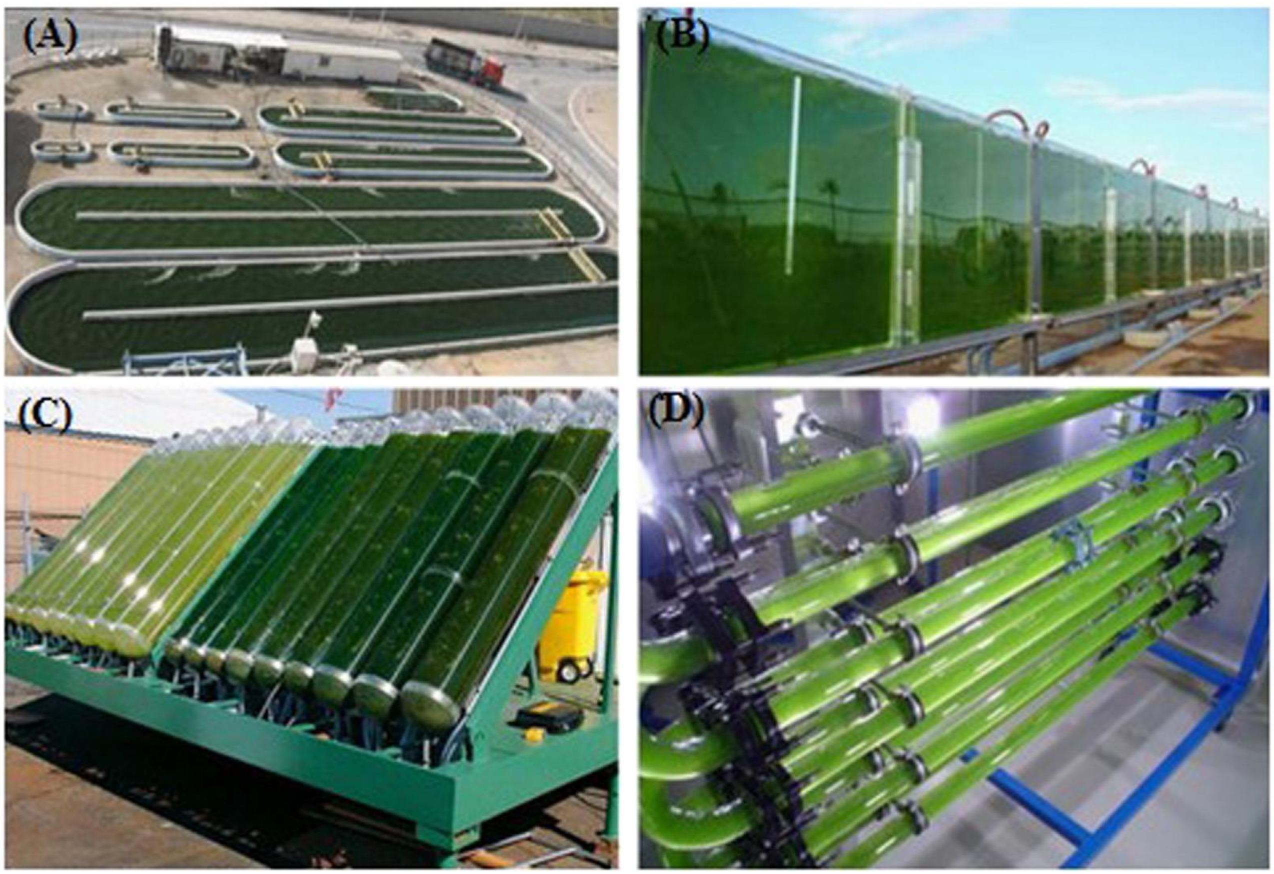

Fig. 3. Cultivation methods for algae (A) natural (B) Cultivation in flat plate photo-bioreactor (C) Cultivation in tubular photo-bioreactor, (D) Cultivation in column photo-bioreactor [79].

CO_2 fixation with wastewater treatment:

Algae production in wastewater is a useful, constructive and sustainable technique in combating environmental pollution. Cultivation of microalgae in wastewater not only sequesters CO_2 from environment as well as solve wastewater discharge related problems partially but also produce various important nutraceuticals , such as β-carotene which can be obtained from the biomass of *Dunaliella* and *Spirulina* species. With an aim to eliminateCO_2 gas from a flue gas stream as well as ammonia from wastewater economically, cultivation of *Dunaleilla*, *Chlorella Vulgaris*were carried out using steel making plant effluent. A CO_2 fixation rate of 26 g. /(m^3.h) and ammonia removal rates of 0.92 gm. NH_3/(m^3.h) were observed when the wastewater was supplemented with 46.0gm PO_4/m^3 at 15% (v/v) CO_2 and with no control of pH condition [80].It has been reported that in Tampa,Howard F. Curren Advanced Wastewater Treatment Plant, and in the city of Lakeland, Florida, the Wetland Treatment System are capable of generating algal biomass of about 71 tons /(ha. year) , liquid biofuel of about 2.7x10^5 gal /hr., and methane of about 4.15x10^6 kg/ yr. [81].

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