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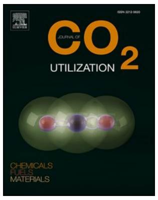

Review Article

Phycocapture of CO_2 as an option to reduce greenhouse gases in cities: Carbon sinks in urban spaces

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ABSTRACT

Climate change is a shift in the average weather patterns, which could stand for a long-term period. This phenomenon is related to greenhouse gas emissions generated by anthropogenic and non-anthropogenic activities. The most notable climate change effects are the rise of sea levels, changes in the water pH, apparition or increased transmission of diseases, changes in the water cycle, loss of marine ecosystems, and several negative impacts on human health. Due to the adverse effects occasioned by climate change, global initiatives have been taken to mitigate its impact, one of these is the reduction of greenhouse gases such as CO_2. Some microorganisms such as photosynthetic bacteria and microalgae can capture CO_2 and use it as a carbon source for growth. The outstanding CO_2 bio-capture or CO_2 phycocapture capacity shown by microalgae make them excellent candidates for reduction of atmospheric CO_2 in cities. CO_2 phyco-capture equivalent CO_2 emissions in Mexico City Metropolitan Area (MCMA) was determined as a case study, considering greenhouse gas emissions in this city. It was estimated that 94,847 tons of microalgae biomass must be produced daily to equal the amount of CO_2 emissions (170,726 CO_2-eq per day), thus obtaining a zero balance of emissions. For the above, CO_2 phycocapture implementation can be possible in cities and also in open spaces and that even its production can work as the carbon credits nowadays implemented, the space required, and the high capture rate led us to consider that the microalgae production on a larger scale may have a faster effect on the concentration of CO_2 globally, which can help with greater urgency to the aims established by 2030.

1. Introduction

Climate change is the variation in the usual weather pattern in some regions; this atypical variation can be determined by analyzing of the historic climate reports, which show changes in the average temperature over an extended time-lapse (decades or longer). This phenomenon, known as global warming, is mainly related to anthropogenic emissions of greenhouse gases (CO_2, CH_4, and N_2O), producing an increase of 0.85 °C in the global temperature from 1880 to 2012 [1]. Besides disruption on biotic and abiotic systems, this temperature variation impacts socioeconomic development globally [2,3]. The anthropogenic activities that produce the most greenhouse gases emission per decade (94,340 thousand metric tons of CO_2) are industrial activities, deforestation, urbanization, burning of fossil fuels, and cement manufacture [4].

CO_2 emission from fossil fuels combustion is the major contributor in global warming, 65 % of global greenhouse gas emissions (74 % of total U.S. anthropogenic CO_2 emissions). The countries that contribute the

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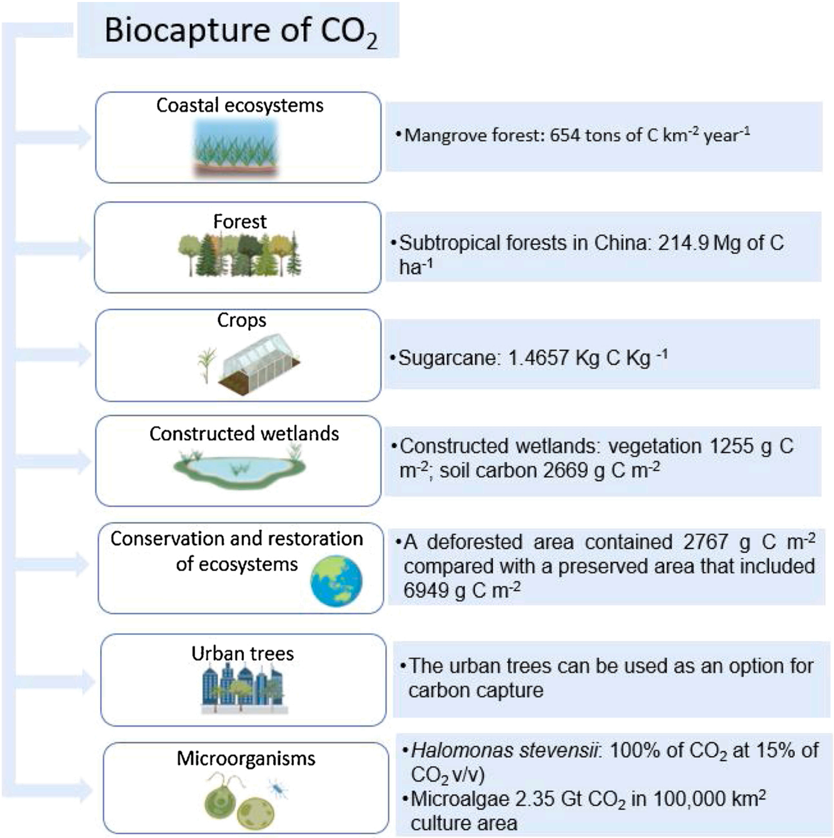


Fig. 1. Types of CO_2 bio-capture or bio-sequestration.

most to CO_2 global emissions from fossil fuel combustion are China, U.S., European Union and India. This is related specially to energy production (25 % of 2010 global greenhouse gas emissions); petroleum burning is the most used source for energy production (2057 million metric tons of carbon dioxide in 2019 produced by U.S) and to electricity production the most used source is coal (782 million metric tons of carbon dioxide in 2019 produced by U.S) [5,6].

Rising global temperatures may expose the population to severe heat waves. Regarding healthy problems triggered by climate change, infection risk is one of the most concerning. For instance, a 0.5 °C rise in temperature can increase 2 times the dengue infection rate and produce an elongation of dengue's season. These temperature changes can also trigger some other dangerous diseases such as malaria and Chagas disease [7–10]. Also, effects on fetal health produced by climate change's effects are well documented [11,12]. For instance, temperatures below to -4 °C and superior than 30 °C are associated with a reduction in birth weight [13]. Environmentally, global climate change produces several risks such as an increase of wildfires occurrence, erosion rate, the vulnerability of mangrove areas, mass extinction of species, an increase of vulnerability of species, species migration to different ecosystems, and invasion of alien species in natural protected areas [14–16]. Furthermore, some other significant effects are the sea-level rise (4.77 mm/year at Uruguayan coast), changes in water pH by the absorption of CO_2 in the ocean, and salinization of groundwater by a salt-water intrusion [1,17,18].

Different studies have shown climate change effects in the hydrologic cycle specifically in rainfall events, and also in infiltration and evapotranspiration rates [19,20]. Due to these, food production (crop yields) has been reduced, producing food security problems [21–23]. For example, some grains' production as wheat can be reduced by 32 % due to the rainfall trend changes [24]. Another food production sector affected by climate change is fishing, due to the loss of marine ecosystems and the biodiversity of marine species [25]. In addition to the food sector, there are other economic sectors that may be affected for climate change such as tourism. The tourism sector has been affected by the loss of natural areas as flora and fauna of attractive places, increased sea levels in coastal areas and degradation of ecotourism attractions [26]. Due to all the global concerns that produce climate change, this phenomenon has been taking importance in different global strategies and programs such as the Kyoto Protocol, the Paris Agreement, and recently, the United Nations' Sustainable Development Goals [27,28]. These actions seek to reduce the climate change, reduce the concentration of greenhouse gases and reduce anthropogenic emissions to these gases into the environment [29,30].

Among the strategies to reduce greenhouse gases emissions from anthropogenic activities are found renewable fuels use and sustainable energy development such as hydrogen fuel use [31]. Nuclear power and geothermal energy have been adopted to dissociate atmospheric CO_2 to hydrocarbon fuels, these CO_2 conversion methods including aqueous electrolysis, thermochemical cycles and electrolysis via molten salts where the formation of CH_4, C_2H_4, C_4H_8, and C_7H_{16} take place [32,33]. The use of biomass to produce energy also is a way to reduce environmental impact from anthropogenic activities because it is used renewable materials for its production. The efficiency of biomass can be enhanced subjecting biomass to pre-treatments methods before its use such as dewatering, drying, torrefaction, densification, size reduction and pelletization [34]. Also, CO_2 capture by chemical processes is a good strategy to reduce greenhouse gases in the atmosphere. For instance, zeolite 13 can efficiently capture CO_2 (95–99 % purity), an approach useful in cement plants [35,36]. Moreover, biological strategies have been followed to CO_2 capture. Generally, these approaches are known as bio-capture or bio-sequestration techniques [37]. Fig. 1 shows the principal bio-capture approaches that have generated interest in academia and among policymakers.

In the present review, CO_2 bio-capture are explored with special insight on phyco-capture and their metabolic mechanisms for CO_2 bio-capture. Furthermore, strategies to enhance their bio-capture potential and possible technologies applied in urban zones are also discussed. Finally, a phyco-capture's case of study in the Mexico City metropolitan area is presented.

2. Types of CO_2 bio-capture

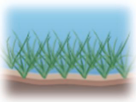
2.1. Bio-capture of CO_2 by natural ecosystems

There are some ecosystems that can capture CO_2. Mangrove forests bio-capture processes can annually capture 654 tons of C per km^2 [38]. Other coastal ecosystems that are excellent CO_2 sinks are seagrass meadows (e.g., *Cymodocea nodosa*) and salt marshes, commonly known as blue C [39,40]. Antarctic coastal ecosystems and the Gulf of Alaska coastal ocean are considered essentials CO_2 sinks, especially during austral summer, storing from 14 to 34 Tg C/yr [41,42]. Also, some studies have shown that the soil and ground biomass in the semi-arid mulga lands of eastern Australia has a CO_2 fixation potential rate of 1.1 t CO_2-e/ha/year [43]. However, due to the loss of some ecosystems, there has been a decrease in the world's C storage, which has caused the world carbon balance to be more negative, encouraging the acceleration in the increase in world temperature. For example, in the Tiantong National Forest Park (China), the forestland decreases its C storage at a rate of 4.38 % annually [44]. It is essential to highlight that these ecosystems' carbon storage is affected by stand age [45], climate, and stand age [46].

Some human activities such as using smart farming techniques, constructing wetlands (well operated), and using some microorganisms in specialized devices can reduce atmospheric CO_2 concentration [47–49]. For instance, some crops can capture CO_2 and can be used for other purposes; the sugarcane can sink 1.4657 Kg C/Kg of vegetable raw material [50]. Constructed wetlands are used as CO_2 sinks. In these constructed ecosystems, its carbon density of vegetation is 1255 g C/m^2, and soil carbon is 2669 g C/m^2 [51]. The restoration of ecosystems is also a useful option to increase carbon storage and its conservation, among these are found both marine and terrestrial ecosystems. A restored mangrove forest has C stock of 42 Mg/ha [52]. The salt marsh ecosystem restoration enhances C capture in these ecosystems, coming to capture 213 g C/m^2/yr [53]. Afforestation initiatives are helpful for carbon sequestration. The program Grain for Green Program in Henan Province enhances low yield sloped cropland, barren hills, and wasteland into forest and grasslands. Due to its activities, the total carbon sequestration rate is 2.47 Tg C/yr, and the total storage in 2012 was 51.73 Tg C [54]. These initiatives promote carbon sequestration, however, they are not enough to equalize carbon emissions in the world.

The international program Reducing Emissions from Deforestation and Forest Degradation and conservation, Sustainable Management of Forests and Enhance of Forest Carbon Stocks (REDD+) enhance sustainable forest management (agroforestry and landscape approaches)in developing countries with actions like conservation and enhancement of forest carbon stocks [55]. Forest ecosystem management can enhance carbon storage by clearcutting and optimizing trees' rotation age, especially in forest plantations [56]. Additionally, these ecosystems' growth positively effects the economy because of the high global demand for harvested wood products. In this way, forest products' trend demand increases the harvest by 17 % in the EU (from 518 Mm^3 in 2015 to 605 Mm^3 in 2030), whence, implementing forest carbon sinks as forest plantation is a good option to obtain an economic income [57]. It is essential to highlight that, although there is a large carbon capture by forest, the harvested wood products manufacture emits CO_2 and methane by combustion [58]. It is important to establish that these systems are limited by the geographic spaces available to establish the initiatives as well as the capture capacity of the biological systems. However, biological carbon capture produces considerable benefits that chemical capture cannot achieve such as the production of organic matter to obtain subproducts and in the case of carbon capture in natural

Table 1
Comparative evaluation CO_2 bio-capturing attributes of different methods.

CO_2 bio-capture method	Advantages	Disadvantages
Coastal ecosystems 	High CO_2 bio-capture rates per phytoplankton Protection of threatened species Protection of vulnerable areas Reduction of the effect of environmental phenomena on the coastal area	Limited areas of application CO_2 bio-capture limited by natural microbiological interactions and eutrophication processes
Forest 	Reduction of species migration due to climate change factors Reforestation of hydrographic basins and greater water catchment Implementation of plantations of timber species Protection of threatened species Protection of vulnerable areas Soil improvement	Limited areas of application CO_2 bio-capture rate limited by the annual growth of the tree and its vegetative stage
Crops 	Production of crops with dual use (Fuel / food) and CO_2 bio-capture	Large areas of land for cultivation Soil wear and salinization Use of pesticides Use of specific crops with good CO_2 bio-capture rate
Constructed wetlands 	Greater water catchment Protection of local species Coupled wastewater treatment processes Soil improvement	Large areas for its application Infiltration of bio accumulative pollutants and emergent contaminants into soil and water reservoirs Use of specific species with good CO_2 bio-capture rate
Conservation and restoration of ecosystems 	Reduction of species migration due to climate change factors Reforestation of hydrographic basins and greater water catchment Use of endemic tree species Protection of threatened species Protection of vulnerable areas Soil improvement Better disease control in ecosystems	Limited areas of application CO_2 bio-capture rate limited by the annual growth of the tree and its vegetative stage
Urban trees 	Use of space in urban areas Improvement of the quality of life of urban residents Landscape improvement	Limited areas of application CO_2 bio-capture rate limited by the annual growth of the tree and its vegetative stage Use of specific tree species consistent with its use in urban areas

(*continued on next page*)

Table 1 (*continued*)

CO_2 bio-capture method	Advantages	Disadvantages
Microorganisms (Microalgae) 	High CO_2 bio-capture rates/ High biomass growth rates Use of space in urban areas Biomass growth in controlled environments Possible use of wastewater for biomass growth Biomass production for biorefinery processes	Limited areas of application

ecosystems, the protection and care of natural areas is crucial for wildlife and endangered species.

2.2. *Possible technologies for CO_2 bio-capture in urban spaces*

In cities, the urban trees can be used as an option for carbon capture, but they can be limited because they increase and lack space in cities. For example, in Singapore, its tropical urban trees' potential to balance anthropogenic emissions of CO_2 is limited and insufficient [59]. The high CO_2 concentration in air and other pollutants can also enhance stomatal closure and decrease city trees' density, such as *Ligustrum lucidum* in Mexico city [60]. Due to the high population rate in cities, the space for the establishment of green areas is limited, therefore, other technologies need to be implemented in order to develop cities with a zero-carbon balance.

Alternatively to vegetal cultures, microorganisms' growth in bioreactors to carbon capture has brought attention [61]. For instance, the bacteria *Halomonas stevensii* can remove 100 % of CO_2 (15 % of CO_2 v/v); in the process, the pH in the experiment changed from 10 to 6.05 in 24 h with a production of fatty alcohols (dodecanol, tetradecanol and pentadecanol) [62]. Microalgae's bioreactors have a great CO_2 mitigating potential. Bio-capture or phyco-capture of CO_2 (phyco-capture is the use of algae to capture into its biomass CO_2 and other contaminants present in the air, soil, and water, this term is related to phyco-remediation, meaning that is defined as the use of algae to treat wastewaters) [63].

Microalgae represent a superior option for carbon fixation than terrestrial plants for higher growth and faster biomass production, doubling their biomass in less than 24 h for most species [64,65]. Microalgae use carbon dioxide for energy conversion while producing approximately half of the atmospheric oxygen [66]. It is estimated that these microorganisms can capture a maximum of 2.35 $GtCO_2$ in 100,000 km^2 culture area [67]. It is suggested that microalgae carbon fixation could be a significant portion of the remaining unidentified carbon sink, which shows the potential of using these organisms to CO_2 capture [68]. The advantages and disadvantages of the application of these CO_2 bio-capture methods are described in Table 1.

3. Phyco-capture of CO_2

3.1. *CO_2 phyco-capture mechanism*

Through photosynthesis (mechanism used by most forms of carbon capture), microalgae can fixate CO_2 by what is known as phyco-capture process. In this process, inorganic compounds and light energy are converted into organic matter by photoautotrophs [69]. Microalgae use light-dependent and light-independent reactions to produce energy (Fig. 2). The first reaction occurring in the thylakoid membranes, and the second reaction in the stroma, both inside the chloroplasts. Through non-cyclic photophosphorylation, electrons are transferred from water through photosystems I and II (light-dependent reactions), where complexes of proteins and pigments harvest light and perform the reactions to obtain NADPH and ATP. The captured energy is then used in the Calvin cycle (light-independent reactions) to produce carbohydrates, such as glucose ($C_6H_{12}O_6$), by using CO_2, and therefore, performing carbon fixation [69–71]. Some microalgae strains can tolerate high CO_2

Table 2
Carbon content (% w/w) of microalgae.

Microalga	CO_2 inlet (%)	Carbon content (% w/w)	Reference
Chlorella vulgaris	10	49	[169]
Chlorella vulgaris	8	45	[110]
Chlorella vulgaris	24	48	[110]
Chlorella PY-ZU1	15	49	[131]
Chlorella fusca	0.03	50	[170]
Pseudokirchneriella subcapitata	0.04	46	[169]
Synechocystis salina	0.04	43	[169]
Microcystis aeruginosa	0.04	42	[169]
Tetraselmis suecica	40	40	[171]
Oscillatoria sp.	100	38	[172]

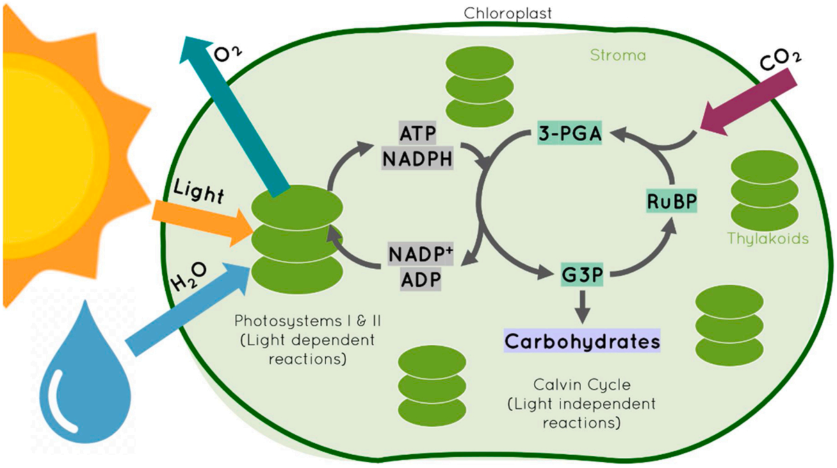


Fig. 2. Mechanisms occurring during photosynthesis. Photosystems I and II occur in the thylakoid membranes through light-dependent reactions using light and water. The Calvin cycle occurs in the stroma through light-independent reactions, using carbon dioxide and generating carbohydrates. 3-PGA: 3-Phosphoglyceric acid. RuBP: Ribulose 1,5-bisphosphate. G3P: Glyceraldehyde-3-phosphate.

concentration (>40 %), such as *Desmodesmus abundans*, *Scenedesmus*, *Chlorella, Micractinium, Picochlorum* [72–77].

For example, *Scenedesmus* sp. has tolerated high concentrations of CO_2; it was reached 2.75 g of biomass per liter at 70 % CO_2, which is a high growth even in optimal conditions (0.03 % CO_2) [73]. Also, each microalga has a carbon content (Table 2) that can guide to determine the potentiality of microalgae to fix CO_2. Broadly, it has been determined that per 1 g of microalgae biomass production, 1.8 g CO_2 is needed [78, 79]. Among the microalgae acclimatization processes to high CO_2 conditions is found the increase of synthesis and accumulation of lipids, and also the increase of pigments synthesis especially Chl *a* and polysaccharide production [80,81]. The use of microalgae for CO_2 biocapture implies other advantages, such as the production of lipids, carbohydrates, proteins, and some other nutrients found in microalgal biomass growth [66,82–85]. These high-value molecules find a transcendental use producing biofuels and food/feed products [86].

3.2. CO_2 phyco-capture potential

Kassim and Meng (2017) showed the CO_2 bio-capture capacity of *Chlorella* sp. and *T. suecica* (CO_2 uptake rate is 95 and 104 mg/L/day by *Chlorella* sp. and *T. suecica*, respectively). Also, it was determined that these microalgae strains could endure high CO_2 concentrations (0.04 %–15 %), being the optimal 5 % for *Chlorella* sp. and 15 % for *T. suecica*. Also, studies have analyzed the cell growth of different microalgae under an increase of CO_2 content (up to 50 %) in the air injected. The results showed that cell growth was given at a rate 3–5 times faster than cultures using normal air [88]. Another study showed that *Chlorella sp.* TISTR 8263, marine *Chlorella* sp. and *C. protothecoides* TISTR 8243. *Scenedesmus obliquus* and *Chlorella pyrenoidosa* grew on media with CO_2 concentrations of up to 50 %. This study also found that *S. obliquus* removed a maximum of 0.288 g L^{-1} day^{-1}, and *C. pirenoidosa* a total of 0.260 g L^{-1} day^{-1} in the presence of 10 % CO_2 [89].

Also, *Grasiella* sp. has been found to capture 0.26 g L^{-1} per day or 18.9 g m^{-2} day^{-1} at conditions of pH 8.0–9.0 (Wang et al., 2018). The microalgae *Arthrospira platensis* (*Spirulina platensis)* have revealed a linear relationship between cell growth rates and CO_2 removal from biogas with an efficiency of carbon fixation for biomass production of almost 95 % [91]. *Euglena gracilis* can remove 64.8 % of CO_2 at an initial CO_2 concentration of 10 %, pH of 3.5, and temperature of 27 °C [92]. *Chlorella* sp. has been shown to remove high CO_2 levels when grown at different CO_2 concentrations. After analyzing different studies, the relationship between the CO_2 concentration in the medium and the CO_2 removal rate seems to be inversely proportional. For instance, for CO_2 concentration of 2% the removal rate was 58 %, for 5% was 27 %, for 10 % was 20 %, and for 15 % was 16 % [93]. This trend is also seen for *Spirulina* sp., achieving a CO_2 capture of 53.29 % and 45.61 % when is grown in 6% CO_2 and 12 % CO_2, respectively [94]. *Nannochloropsis oculate* grown also at different CO_2 concentrations of 2%, 5%, 10 %, and 15 % achieved a CO_2 removal of 47 %, 20 %, 15 %, and 15 % respectively [95]. *Scenedesmus obliquus* removed 28.8 % of CO_2 in a culture media with 6% CO_2, and 13.56 % in 12 % CO_2 [94]. Other examples of CO_2 phyco-capture are expressed in Table 2.

The microalgae strains *Dunaliella tertiolecta*, *Chlorella vulgaris*, *Thalassiosira weissflogii*, and *Isochrysis galbana* can grow and capture CO_2 from emissions of the cement industry. However, in this process, dust concentrations of cement gases may inhibit microalgae growth. Therefore, it must be removed before being injected into microalgae culture [96]. Some of the CO_2 phycocapture studies were done with wastewater as a culture media, making a complete phycoremediation process [97–99]. Also, *Chlorella sorokiniana* UKM2 strain was grown in palm oil mill effluent (10 % v/v) aerated with 1% (v/v) CO_2, and it was determined a CO_2 uptake rate of 567 mg/L/day, obtaining a microalgae growth of 1 g/L on day 5 of culture. Also, 100 %, 65 %, and 56 % of NH_4^+, total nitrogen (TN), and total phosphate (TP) were removed, respectively [100]. Similarly, treated chemical wastewater (purified terephthalic acid wastewater) can be used as culture media, obtaining an algal CO_2 capture rate of 91.59 % with a 10 % CO_2 supply [101].

Kitchen wastewater and sewage wastewater have also been treated with microalgae. For example, *Chlorella* reached biomass productivity of 0.6 g/L using sewage wastewater as a culture medium with a flue gas supply (6% CO_2, SOx180 ppm, and NOx250 ppm) [102]. Also, there have also been studies where the removal of emerging pollutants in wastewater has been demonstrated by microalgae [103]. For instance, Cheng et al. (2018) found that *Chlorella PY-ZU1* removes 95 % of ethinylestradiol (Initial concentration: 5 mg/L) from wastewater with a 15 % CO_2 supply. Also, antibiotics such as amoxicillin and cefradine in wastewater can be removed by microalgae with 10–30 % CO_2 supply [105]. Microalgae also are used in bioremediation of wastewater with heavy metals (As, B, Cu, Mn, Zn, among others). However, this process, particularly the CO_2 concentration supply, can affect heavy metals removal [106].

The process of phyco-capture of CO_2 in wastewater is an example of a circular economy by obtaining by-products from waste. For example, *Scenedesmus* sp. culture in domestic wastewater supplemented with 2.5 % CO_2 produced 196 mg of biomass/L/day with lipid content of 33 % and achieved a CO_2 consumption rate capture of 368 mg/L/d. Among the biomass's lipid composition, FAME (saturated and unsaturated fatty acids) were found and determined to be potentially applicable for biodiesel production [107–109]. Another critical highlight from these studies is the importance of maintaining the N:P ratio in 10:1 to generate high amounts of microalgae biomass and lipids [110]. Also, biofuel production can be pursued since many microalgae increase their lipid accumulation when the carbon to nitrogen ratio is increased [91]. For example, high CO_2 levels (30−50%) resulted in the best carbon dioxide concentration for the production of total lipids and polyunsaturated fatty acids in *Scenedesmus obliquus* SJTU-3 and *Chlorella pyrenoidosa* SJTU-2 [89]. *Chlamydomonas* sp. JSC4 cultivated with 8% CO_2 supply may have a lipid composition of 46 % of C16:O, 21 % of C18:0, and 13 % of C18:1 [111].

Chlorella vulgaris growth in treated wastewater with 15 % CO_2 supply reached lipid productivity of 0.164 g lipids/g cell/day with 44 % of oleic acid content [112]. In addition to lipids' production, some pigments can be extracted from microalgae biomass obtained from CO_2 phycocapture process, for example, *Thermosynechococcus* sp. CL-1 can produce 0.074 mg/L/h and 0.39 mg/L/h of zeaxanthin and β-carotene, respectively [113]. Also, from CO_2 phycocapture process, it can be obtained an income of $440–1028/ton of microalgae biomass produced [114]. Some studies, where besides CO_2 capture by microalgae may be removing the heavy metals such as Al and Fe presented in flue gas [115]. Furthermore, using microalgae biomass for heavy H_2S, SO_2, and NO removal from coal combustion has been applied [116–118]. Demonstrating that microalgae for CO_2 bio-capture can also provide cleaner air to the atmosphere without heavy metals [115].

3.3. Strategies to enhance CO_2 phyco-capture potential

There are some strategies to ensure good results in the CO_2 phycocapture process, such as using a tolerant CO_2 strain, implement a combined chemical-biological CO_2 capture process such as using polyethylene glycol 200, diethanolamine, pentoses (xylose and arabinose), adding CO_2 absorbents such as potassium carbonate to promote microalgae growth, modifying the growing temperature, superficial gas velocity, gas flow rate, and CO_2 inlet concentration [88,119–126]. Highlighting the use of $NaHCO_3$, which improves CO_2 fixation efficiency in a range of 82%–99% [127]. It is essential to consider the light intensity because the light penetration in the bioreactor will be reduced with the microalgae growth process, decreasing microalgae cell growth [128,129]. Moreover, the literature recommends maintaining the light intensity in 4500 lx (1200–1600 μmol m^{-1} s^{-1}). These values must also be evaluated for each microalga [88,130]. For instance, *Chlorella* PY-ZU1, by increasing light intensity from 4500 to 6000 lx, increased its

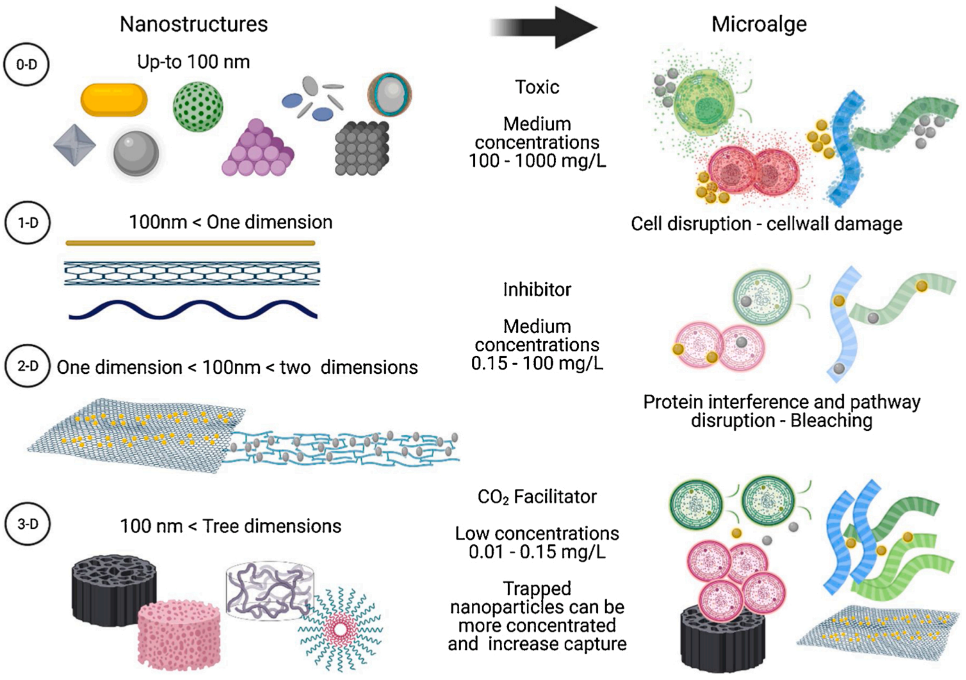


Fig. 3. Strategies to aid microalgae CO2 bio-capture by nanotechnology.

growth and CO_2 fixation efficiency [131].

Furthermore, control the aeration's bubble size is necessary to increase biomass production and CO_2 dissolution [132]. Also, the use of some instruments to increase mass-transfer CO_2 to culture medium can be useful. For example, the use of a single helical baffle in microalgae culture increases 23 % algal biomass; also this promoted homogeneity distribution of nutrients because of the spiral flow generated [133]. The use of micro-bubbles aerator can also enhance CO_2 mass-transfer to the culture medium. Excellent results have been seen using a round gas distributor with holes with an inner diameter of 0.5 mm and spacing of 1.5 mm [134].

It is possible to explore some nanotechnology tendencies applied to CO_2 bio-capture (Fig. 3**)**. Nanoparticles used as additive in microalgae cultivation can improve the CO_2 bio-capture and make more efficient photoconversion. The most limiting factor to apply nanoparticle additives is related to the microalgae toxicity which must be evaluated for each specific set of microalgae and nanoparticles. Toxicity factors include the nanoparticle characteristics such as size, material, oxidation state and crystal structure, the concentration, media interaction and microalgae strain. Other studies were carried out using different strains and nanoparticles presented elsewhere [135]. Here it is discussed the successful cases the combination of *Chlamydomonas reinhardti* with Cr_2O_3 nanoparticles at 100 mg/L [136]. Other with the same strain and CuO at three concentrations 0.1, 1 and 10 mg/L [137], similarly the use of AgNP (30−50 nm) between the concentrations of 0.01 to 0.15 mg/L [138]. This includes the nanoparticle type and material used, additionally to the nanostructure applied. In general, the nanoparticles can positive or negatively affect the microalgae culture depending on the concentration and degree of freedom for their direct interaction. A successful example is the use of nanofibers containing nanoparticles with CO_2 capture potential (e.g., nanofibers with $NPsFe_2O_3$ that has a CO_2 adsorption capacity of 164.2 mg/g), also the use of these nanofibers can increase lipid production, helping by this way the production of by-products of interest [139,140].

It is important to know that the CO_2 supply in microalgae cultures affects pH; this reduction affects the nutrient uptake and, consequently, the microalgae growth. Also, the pH reduction can allow the contamination of the microalgae culture with bacteria and fungi. Consequently, monitoring pH is essential in the CO_2 bio-capture process by microalgae [87]. It is important to highlight that the highest conversion of CO_2 into carbon biomass was observed at pH 7 [141]. Regarding industrial flue gas use, this can be directly introduced into the microalgal cultures without any pretreatment, producing a pH decreases in the culture medium, an increase in the temperature, and dissolution of nitrogen oxides and sulfur oxides present. Although extremely low pH and acidic gases have fatal effects on higher plants, some microalgae survive these conditions and capture CO_2 [142]. The acidification of culture medium by the effect of the CO_2 supplied may have a chain reaction on the microalgae physiology. For example, CO_2 acidification on *Tetraselmis* sp. may induce a lower conversion of light to chemical energy because it affects the microalgae photosynthetic metabolism [143]. A successful alternative is to capture and purify the industrial flue gas to be administered to microalgal cultures at desired concentrations [64], making tolerable conditions for most microalgae.

4. Possible technologies for phyco-capture of CO_2 in urban spaces

Phyco-capture of CO_2 is an option to improve air quality in urban spaces and reduce greenhouse gas concentration in the atmosphere, creating a CO_2 sink type in areas where it produces a large percentage of these gases in the world by anthropogenic activities. This proposal is based on microalgae's potential to improve air quality by capture CO_2 and other air contaminants. Also, the main objective is creating carbon neutrality between CO_2 emissions from everyday activities in a city and the CO_2 phyco-capture process. As we mentioned in the previous section, microalgae have great potential in greenhouse gas capture especially in CO_2 capture. However, critical infrastructure is needed to achieve this goal. Among these needs, a properly bioreactor design to ensure the most CO_2 phyco-capture in the smallest possible space where the bioreactors are spotted. Regarding the possible microalgae strain to use, it is recommended to use one with high CO_2 tolerance and CO_2 capture capacity, as shown in Table 4.

On the other hand, the bioreactor design has several issues that must be considered, such as the space it occupies, the volume of culture, and the ease of operation. Currently, there are some studies where microalgae are grown on large scale. In some cases, these projects aim has been CO_2 phyco-capture; however, this potential is not studied in depth. Among the bioreactors types for microalgae culture are found open pounds, airlift bioreactors, manifolds reactors, and serpentine bioreactors. The microalgae cultivation can be done, depending on whether or not they are directly exposed to the atmosphere, in open pond bioreactor and closed bioreactor. In open-pond systems, the most outstanding characteristics include simple construction, low cost, and easy operation. However, some disadvantages are high evaporation loss, low light utilization by the cells, difficulties for operation control, high risk of contamination, low biomass density and low CO_2 sequestration rate. The open systems include ponds, lagoons, deep channels, shallow circulating units, and others [144,145].

Raceway open pounds are bioreactors that can be used for microalgae cultivation. They commonly are systems that generate low microalgae biomass, but they have low capital and operating costs for large-scale cultures. These systems are found in many dimensions depending on the space available for construction. When is needed to supply CO_2 in these systems is done by pipeline gas system ensured gas delivery in aeration zones sometimes equipped with a gas diffuser. Most of the wastewater treatment with microalgae is made in these systems, is possible that the supply CO_2 enhances microalgal biomass production [146,147]. High-rate ponds (HRPs) also are used for microalgae cultivation. For instance, a pilot-scale with HRPs for wastewater treatment by microalgae was implemented. The HRPs were made of fiberglass with six-blade steel paddles; they had the following characteristics: width of 1.28 m, length of 2.86 m, total depth of 0.5 m, the surface area of 3.3 m^2, and sound volume of 1 m^3. The cultures were supplied with 99 % and 5% CO_2. The CO_2 supply was carried out in the lower part of the HRPs, through a carbonation column as a gas diffuser, and allowed a more significant contact time of the gaseous CO_2 with the culture. These systems was monitored pH, temperature, dissolved oxygen, photosynthetically active radiation, and *Escherichia coli* presence [148]. Open raceway ponds are usually used for microalgae biomass production. For instance, *Spirulina platensis* has been cultivated in this type of reactor with a capacity of 14,000 L for biomass, proteins, and pigments production (phycocyanin). It was demonstrated that CO_2 supply provides a carbon source and can be used to control culture pH [149].

Other options to use as microalgae bioreactor closed systems have many advantages, including easy control, insufficient space required, high CO_2 sequestration rate, and no contamination risk, nearby all microalgae species may be cultivated, and high biomass density. Nevertheless, closed systems' major limitations are high investment cost, high operation cost, and scalability difficulty. The commonly used closed photobioreactors include tubular, flat panel, cylindrical airlift photobioreactors, stirred fermenters, and bag reactors [144,150]. Another option to use as a microalgae bioreactor is to use of conical transparent polyethylene bags with bubble columns with a capacity of 25 L, a microalga consortium was growing in this system for heavy metals capture from coal-fired flue gas with 5.5 % of CO_2. It was found that B, Mn, and Zn were found in the microalgae cells during the cultivation period, concluding that microalgae may offer a solution for the heavy metal pollution in the air [115]. In this system also it was determined that high CO_2 concentration supply (>5% CO_2) showed lower saturated fatty acids unsaturated fatty acids present, which can reduce the viability of using this microalgae biomass for biodiesel production [151].

Table 3
Phyco-capture of CO_2.

Microalgae	CO_2 influx (%)	Phyco-capture of CO_2 (%)	Reference
Chlorella sp. UKM2	1	567[a]	[100]
Chlorella sp.	10	35	[173]
Chlorella vulgaris	10	98	[174]
Chlorella vulgaris	10	3.3[b]	[161]
Chlorella vulgaris	11	15	[175]
Chlorella vulgaris	10	127 [a]	[169]
Chlorella vulgaris	2	80	[176]
Chlorella vulgaris	5	0.339 [b]	[177]
Chlorella vulgaris	10	0.322 [b]	[177]
Chlorella vulgaris	15	0.315 [b]	[177]
Chlorella vulgaris	20	0.310 [b]	[177]
Chlorella regularis var. *minima*	10	32	[173]
Chlorella fusca LEB 111	10	360 [a]	[178]
Chlorella PY-ZU1	15	32	[179]
Chlorella sp. *L166*	5	25	[180]
Chlorella sp. *L166*	10	19	[180]
Chlorella pyrenoidosa	5–15	0.209 [b]	[181]
Chlorella minutissima	10	250[a]	[126]
Chlorella minutissima	20	274[a]	[126]
Scenedesmus obliquus	10	95	[174]
Scenedesmus obliquus	10	2.34[b]	[161]
Scenedesmus obliquus CNW-N	2.5	1030[a]	[125]
Scenedesmus dimorphus	10	94	[174]
Scenedesmus dimorphus	0.64[b]	78	[182]
Scenedesmus obtusiusculus	3.8	5.6	[183]
Scenedesmus sp.	10	6.6	[49]
Scenedesmus sp.	20	5	[49]
Chlorella sp.	5	0.1	[124]
Spirulina sp.	5	155 [a]	[184]
Spirulina sp. LEB 18	10	135 [a]	[178]
Spirulina platensis	2.5	62	[185]
Synechococcus nidulans LEB 115	10	55	[186]
Tetraselmis suecica	5	111[a]	[87]
Tetraselmis suecica	15	104[a]	[87]
Tetraselmis suecica	30	4.81[a]	[87]
Tetradesmus obliquus PF3	10	718 [a]	[187]
Desmodesmus abundans	25	335[a]	[188]
Monoraphidium contortum	10	1.4[b]	[161]
Nannochloropsis gaditana	30	96	[189]
Oscillatoria sp.	100	156[a]	[172]
Psammothidium sp.	10	3.2[b]	[161]
Pseudokirchneriella subcapitata	10	54[a]	[169]
Botryococcus braunii	10	6.78	[49]
Botryococcus braunii	20	20.7	[49]

[a] mg CO_2/L/day.
[b] g CO_2/L/day.

Cylindrical photobioreactors act as an airlift bioreactor also can be used for CO_2 phyco-capture purposes, where the bottom of the bio-rector can supply CO_2. For example, for the cultivation of *Chlorella vulgaris* MSU-AGM 14, it was used cylindrical photobioreactors of 30 L with a 4% and 8% CO_2 supply, it was determined that CO_2 supply promoted biomass and lipid productivity [152]. In the use of this type of bioreactors, it has been shown that it is essential to control superficial gas velocity, as the CO_2 removal efficiency capacity can be increased at a gas velocity of 1.88×10^{-3} m/s, and also can enhance biomass productivity [120]. It was analyzed that airlift bioreactor design required a more significant amount of operating energy than raceway pond. In the case of the first it is needed 3.21 MJ/Kg of biomass and in the raceway pond is needed 1.15 MJ/Kg of biomass, which means that twice as much energy is used in airlift bioreactor, however in this, a more outstanding biomass amount was produced, and therefore it is expected a greater CO_2 phyco-capture capacity [153].

Horizontal tubular photobioreactors can also be used for CO_2 phyco-capture; remarkably, these systems consist of thin tubular placed horizontally to allow a greater incidence of light in the culture. These systems are similar manifolds reactors and serpentine bioreactors. In this kind of system, the use of CO_2 microbubbles dissolvers at the gas inlet to enhance the CO_2 dissolved and biomass production in the culture medium, reducing bubble formation diameter [154]. Other types of bioreactors used for microalgae cultivation are the laminar photobioreactors or microalgae biofilm photobioreactors. They consist of a vertical chamber covered on both sides with fabric (polypropylene geotextile) sheets of $1.5 \times 2 \times 0.10$ m size, a water recirculation system, and a mixing tank. This type of bioreactors is based on some microalgae strains' capacity to grow as biofilm; species such as *Chlorella* spp. and

Table 4
Phyco-capture of CO_2 in great scale (Cultures > 50 L).

Microalgae	Volume (L)	Reactor	% CO_2 influx	% CO_2 Phyco-capture	Reference
Chlorellasp. MTF-7	50	Bubble colum	23 ± 5	60	[190]
Chlorella vulgaris	60	Raceway pond	10	102[a]	[146]
Chlorella vulgaris	60	Raceway pond	0.04	13.9[a]	[146]
Synechocystis aquatilis SI-2	72	Flat-plate	10	51[c]	[191]
Scenedesmus sp. and *Chlorella* sp	200	Raceway pond	20	24.6[b]	[192]
Mixed indigenous microalgae	250	Columns operating in series	10	0.542–1.075[e]	[193]
Chlorella sp. AT1	528	Photobioreactors Raceway circulating	2	64	[194]
Phormidium valderianum BDU 20,041	550	Cylindrical tank	15	56.4[d]	[79]
Arthrospira sp	900	Tangential spiral – flow column photobioreactors	15	0.358[b]	[195]
Graesiella sp. WBG1	1000	Raceway	15	0.23[b]	[90]
Chlorella pyrenoidosa (FACHB 9)	8000	Bubblying colum	5–10	11.17	[196]
Chlorella pyrenoidosa (FACHB 9)	8000	Spraying absorption tower with an open raceway pond	99.50	50	[196]
Tetraselmis sp. CTP4,	100,000	Horizontal tubular photobioreactor	13.67[f]	60–75%	[197]
Spirulina sp.	206,000	Double paddlewheels, baffles, and aerator raceway pond	99	79.4	[198]
Nannochloropsis oculata	310,000	Raceway pond	11–14	11–24	[199]

[a] mg CO_2/L/day.
[b] g CO_2/L/day.
[c] CO_2 /m2/day.
[d] mg C/L.
[e] g C/L/day.
[f] kg/day.

Scenedesmus spp. were used in these systems. CO_2 can also be supplied to these cultures, it can be supplied inside the chamber, and in this bioreactor, the moistened fabric prevents CO_2 leakage from the system. Among these systems' advantages are the constant exposure of the microalgae to incident radiation and the high biomass production [155]. Microalgae biofilm photobioreactors can also be used to *Scenedesmus obliquus* culture; the roughness of substratum surface for biofilm adhesion was used and improved in 28 % biomass density, showing the importance of substrate adhesion capacity in these systems. With these properties, 65 % CO_2 removal efficiency can be achieved with a gas inlet of 10 % CO_2 [156].

It is recommended that bioreactors must have a monitoring system for some variables such as light, pH, and dissolved CO_2. As it was mentioned in the previous section, pH is a variable essential in CO_2 phyco-capture process. For example, a microalga consortium (*Chlamydomonas* sp., *Nannochloris* sp. and *Chlorella stigmatophora*) grown in a high-rate algal pond of 4.46 m^3 (surface area of 10 m^2) reaches the highest conversion of CO_2 into microalga biomass at pH 7 in that case. Especially in open bioreactors, is needed to consider the possible presence of microalgae depredator in the culture such as protozoans and

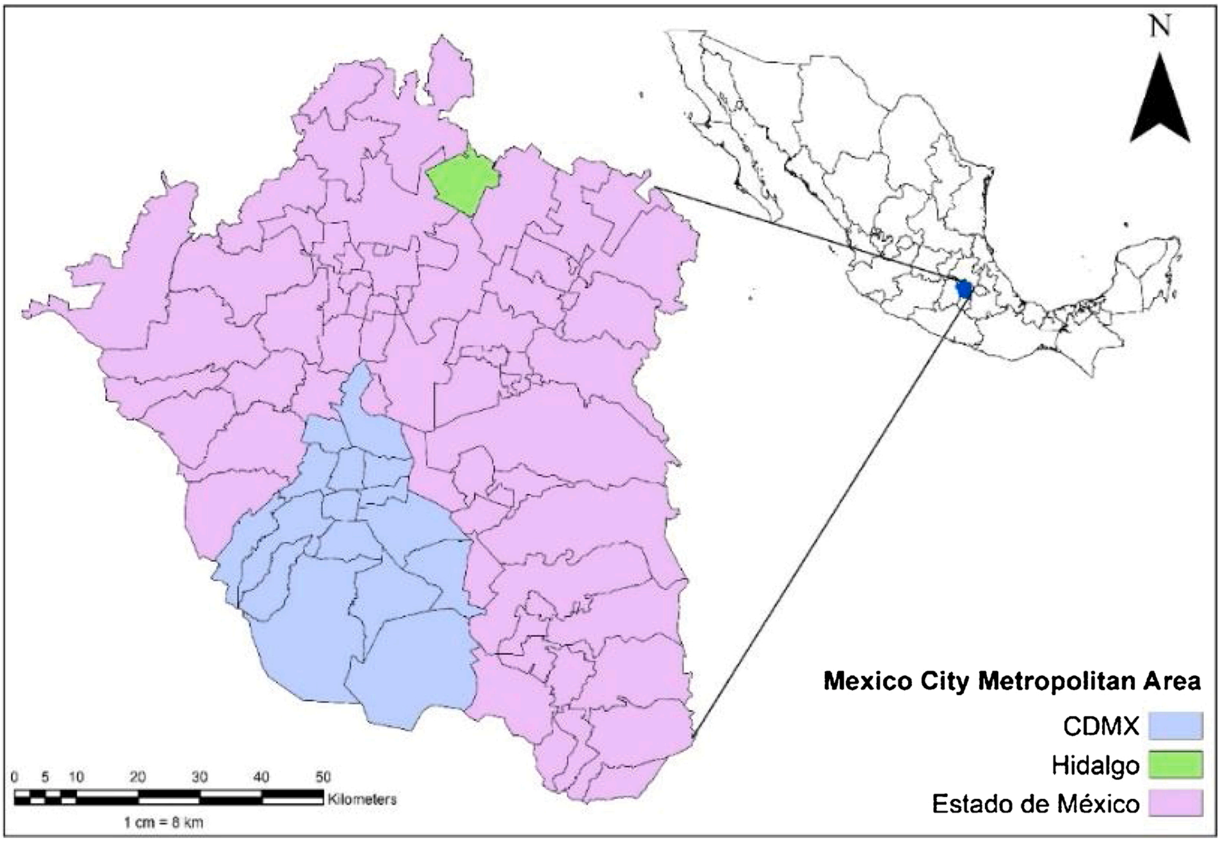


Fig. 4. Geographical location of Mexico City Metropolitan Area divided by zone. Data source: [168].

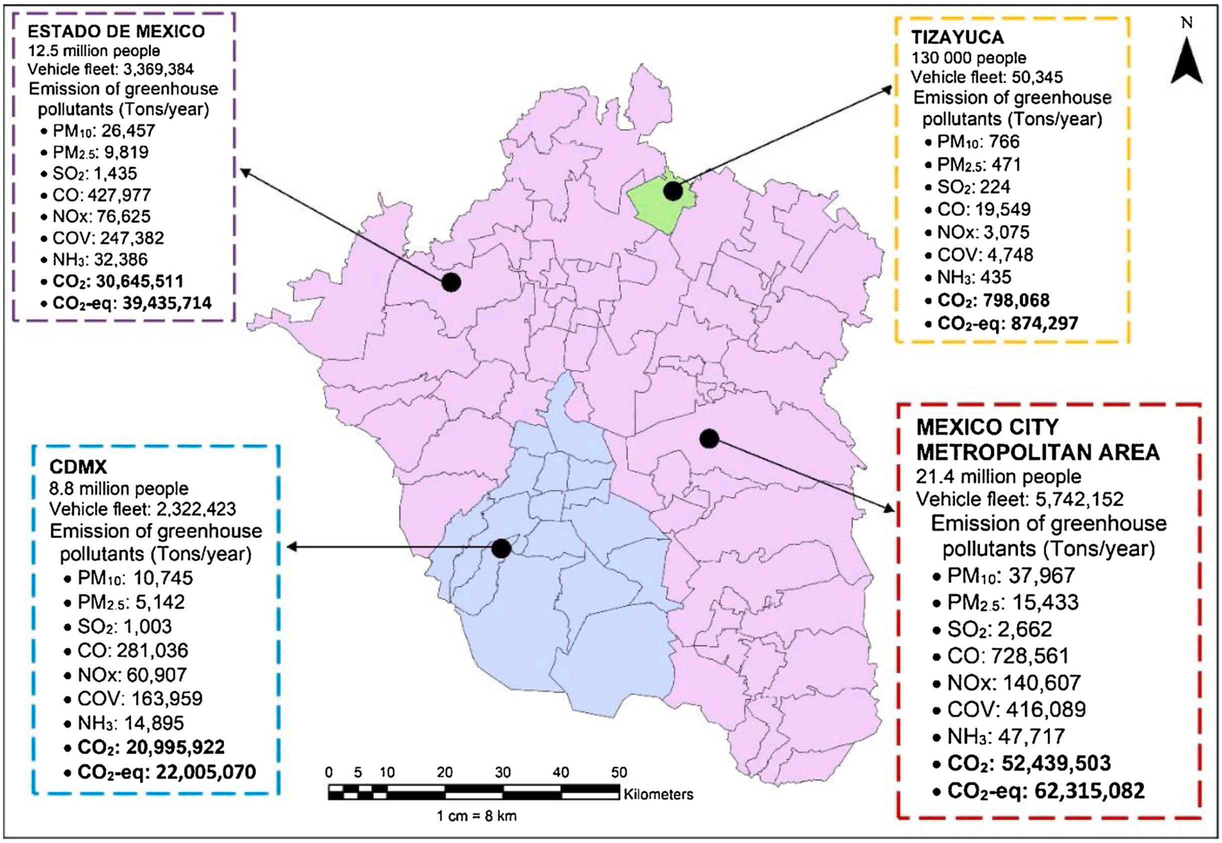


Fig. 5. Total emission related with greenhouse gases of Mexico City Metropolitan Area by zone. Data source: [158,168].

metazoans species. This presence can affect microalgae growth and, in some cases meaning the total loss of culture [141]. Recently, studies have developed the processes and technologies to apply microalgae on an industrial scale. However, the transition from pilot-scale operations to industrial-scale operations often exposes microalgae cells to harsh circumstances, resulting in reduced product production. Thus, several innovative technological solutions are still needed to exceed their satisfactory performance to achieve commercial viability. In this context, photobioreactors' use to perform microalgae-based processes prompted the development of different reactor configurations to achieve scale characteristics proportional to industrial demands [157]. Table 3 shows some examples of CO_2 phyco-capture on a significant scale.

5. Case of study: CO_2 phyco-capture potential in Mexico city Metropolitan Area

Regarding the microalgae potential to CO_2 capture, it was determined the CO_2 phyco-capture potential in Mexico City Metropolitan Area (MCMA) as a case of study to show the most significant opportunity that have the implementation of phyco-capture processes in cities, under the premise of capturing the same amount of emissions (CO_2-eq) that a city generates. MCMA is integrated by 3 states of Mexico: Mexico City (CDMX), Estado de Mexico (59 municipalities) and Hidalgo (Tizayuca municipality) (Fig. 4). MCMA is the most populated geographic zone of Mexico, with 21.4 million people. It was determined by Secretaría del Medio Ambiente de la Ciudad de México (SEDEMA) the total emission-related with greenhouse gases of MCMA, taking into account different anthropogenic activities as mobility, economic activities, among others, and it was considered punctual and non-punctual emissions. It was determined that the total emission of CO_2 is of 52,439,503 Tons/year, and the total emission of CO_2-eq is of 62,315,082 Tons/year in MCMA (Fig. 5). These emissions are mostly because of its vehicle fleet made up of 5,742,152 vehicles, which provide 32,323,570 Tons/Year/CO_2-eq, representing at least 50 % of total emissions in this geographical area [158]. Other significant sources of greenhouse emissions are landfills use, industrial and home combustion processes, generation, transmission and distribution of energy and generation of goods and services. The CO_2 phyco-capture necessary to equal the equivalent CO_2 emissions in MCMA was determined, considering greenhouse gas emissions. It is estimated that 94,847 tons of microalgae biomass need to be produced daily to equal the amount of CO_2 emissions (170,726 CO_2-eq per day), thus obtaining a zero balance of emissions cultivation volume of 0.22 km^3 (Fig. 6).

Mexico has a microalgae culture potential of 526,672 km^2 (26.8 % of the country), considering land characteristics and resources (land use, topographic slope, temperature, evaporation, solar radiation, vegetation, water, and CO2 sources. Microalgae cultivation areas in different locations of Mexico are as follows: 21,243 ha in Mexico City, 563,521 in Estado de México, and 567,830 in Hidalgo, the spaces determined by this model and other spaces that can be used increased the possibility to use this CO_2 capture method [159]. One of the biggest concerns to produce biomass is the land use for this purpose. Thus, one of the ways to reduce land use is the construction of reactors that allow producing more biomass in less space, such as optimized open pounds, airlift bioreactors (vertical column photobioreactors), sequential bioreactors, and manifold bioreactors [131,144,160,161]. These reactors can be implemented in avenues that have a space for green areas, in green areas previously established, such as parks, some known as the city's lungs, in under-exploited spaces, and wastewater treatment plants [148]. Its installation in future infrastructure projects and land use plans can also be considered (Fig. 7). Also, microalgae strain with high carbon content and accelerated microalga growth can enhance CO_2 phyco-capture in less space, improve the transfer of CO_2 to the culture medium by regulating flows, and reducing the size of bubbles and optimize the light intensity according to the microalga strain used. One of the strategies that can be implemented is to increase CO_2 inlet concentration by used

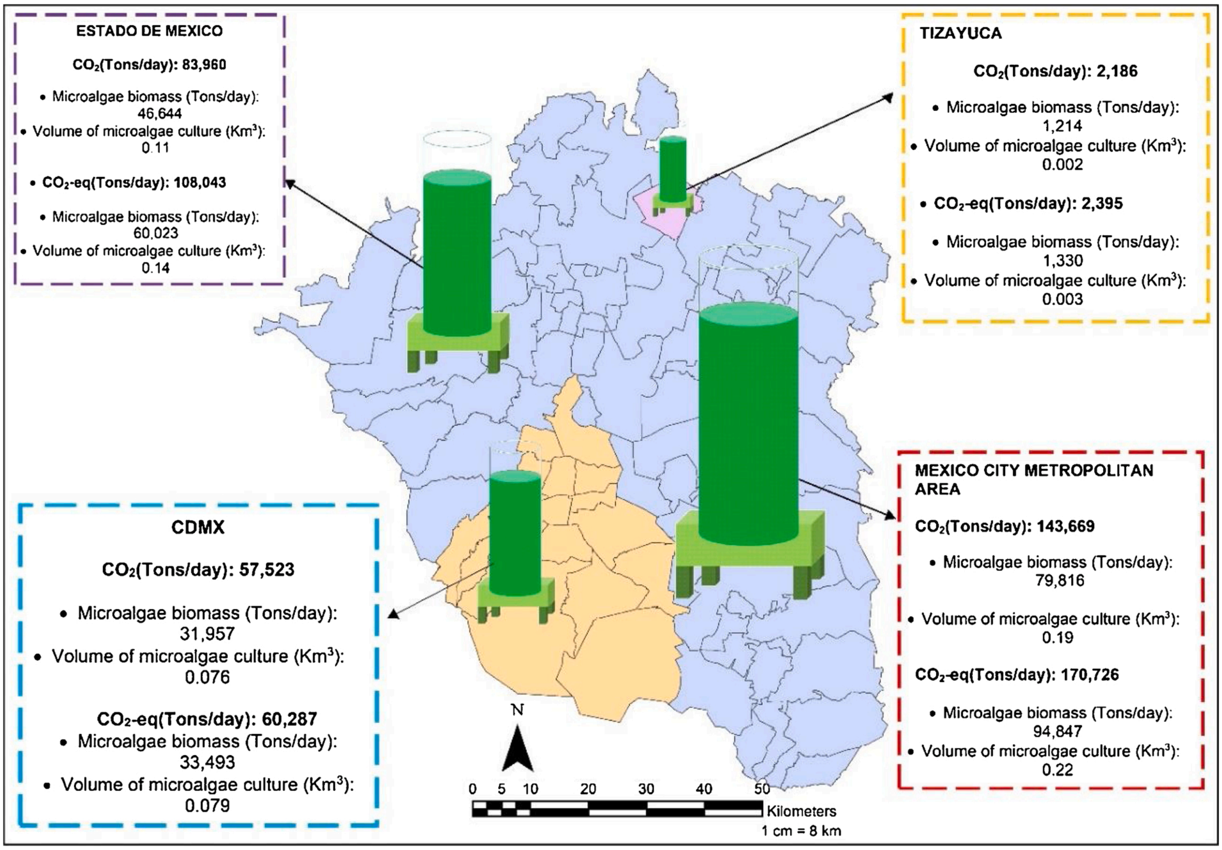


Fig. 6. Phyco-capture needed in Mexico City Metropolitan Area considering total emission related with greenhouse gases by zone. It was considered that to produce 1 kg of microalgae biomass it is needed 1.8 kg of CO_2. Data source: [158,168].

some chemical absorption processes to obtained CO_2 concentrated from the air or use industrial flue gas [162–164].

5.1. Cost-effective aspects

It was estimated that per m^3 of culture installed in a CO_2 phyco-capture plant, it needed an investment of 3350 $USD (817 $USD per tCO_2-eq/year: Considering 5 years of operation) [165]. In the case of the use of mangrove blue for CO_2 capture is needed 9 $USD per tCO_2-eq/-year [166], however, the areas of application are limited and are not enough to capture all the CO_2 generated in the world. In the case of implementation of plantations of timber species the costs oscillate between 10 $USD to 68 $USD tCO_2-eq and 25 $USD tCO_2-eq in reforestation implementation [167], although the implementation costs are low, the space required and CO_2 capture rate makes this a difficult option to apply it, more considering the projected global climate change scenarios that propose to look for different greenhouses gases capture methods. These methods have to be more effective and faster, for the little time estimated that exist to change this situation without affecting the current lifestyle of the human being.

For phyco-capture process, the most effective option to reduce production cost is to use the land adjacent to wastewater treatment plants, where this waste can generate biomass as a culture medium. Besides, wastewater can reduce the amount of clean water needed for microalgae production [86]. Also, it can be used strains with more CO_2 capture potential, obtaining more CO_2 capture in less space and reduce the input costs. Also, biomass production can be used to produce subproducts such as pigments production, bioplastics, biofertilizers, biodiesel, and animal nutritional supplements, generating a circular economy process and an economic income [86].

6. Perspectives and challenges

Climate change has on world agendas, and its consequences make it a priority issue for their attention. The search for methods to capture greenhouse gases is of vital importance to the environment and human lifestyle. The bio-capture of CO_2 by microalgae is an excellent candidate to be implemented in the world. On large scales, these systems can function like the current carbon credits implemented in forest zones, where the systems capture the CO_2 equivalent to the emissions of human activities not precisely carried out in the broadcast area. This way of capture can guarantee a greater capture efficiency than that carried out with higher plants, where this system can capture more than 15 times what is captured by an average tree. Also, because these systems must be implemented in bioreactors, these can be established in different areas. In cities, CO_2 phycocapture process can be implemented as bioreactor parks, using land dedicated to green areas, neighboring lands to wastewater treatment plants or be included in new land utilization plans. Although carbon credits implemented in forest spaces are so useful, the space required and the low capture rate led us to consider that the growth of microalgae on a larger scale may have a faster impact on the concentration of CO_2 globally, which can help with greater urgency to the aims established by 2030. Also, the CO_2 captured by microalgae could be considered for inclusion in carbon markets.

CRediT authorship contribution statement

Itzel Y. López-Pacheco: Conceptualization, Data Analysis, Figures, Tables, Writing-Original Draft; **Laura Isabel Rodas-Zuluaga** and **Susana Fuentes-Tristan:** Data Analysis, Writing-Original Draft. **Carlos Castillo-Zacarías** and **Juan Eduardo Sosa-Hernández:** Writing-Original Draft; **Damià Barceló** and **Hafiz M.N. Iqbal:**

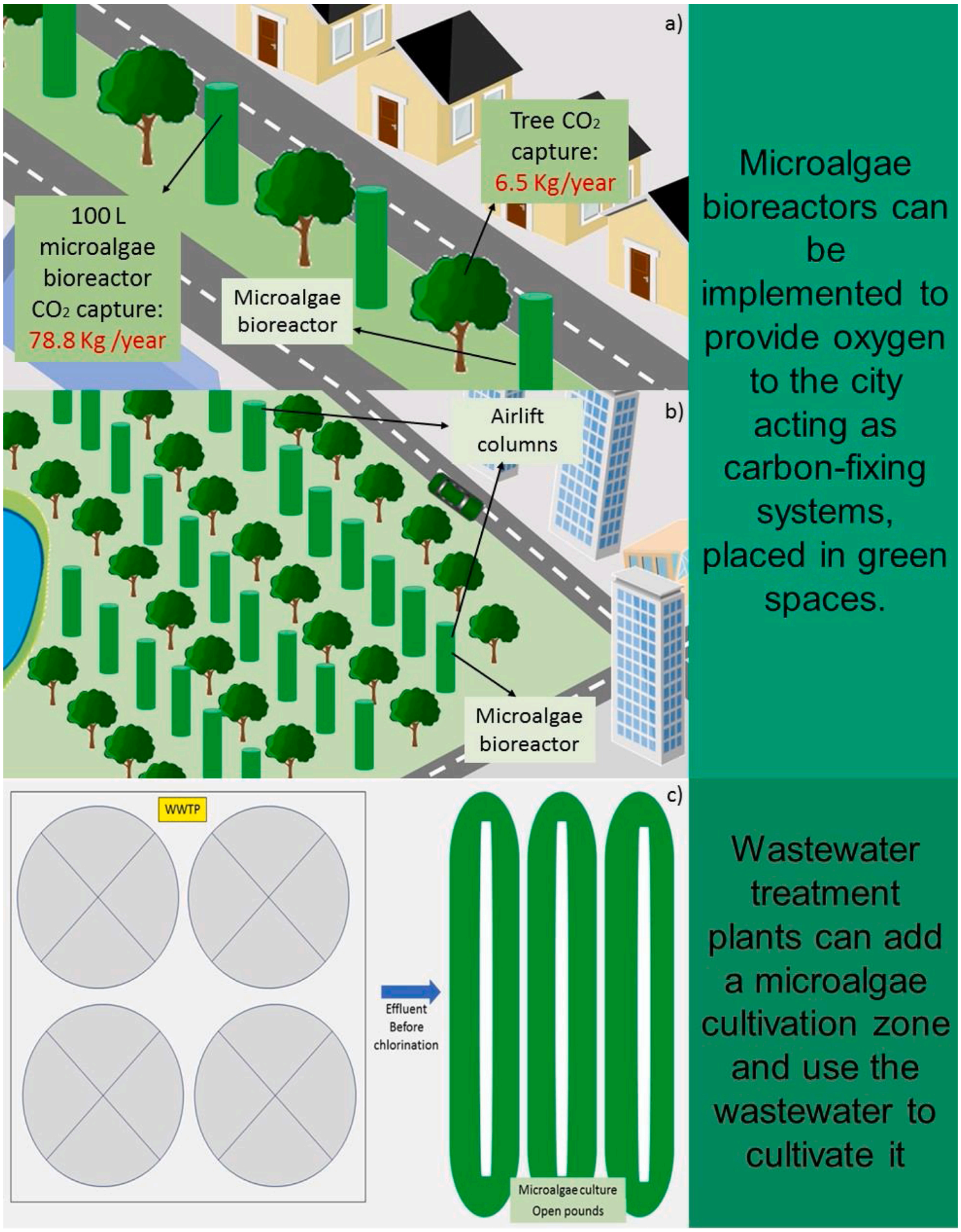


Fig. 7. Possible ways to implement bioreactors for CO_2 phyco-capture process in cities. a) Implementation of bioreactors in avenues with green areas, b) Implementation of bioreactors in green areas such as parks and boardwalks, c) Implementation of bioreactors in WWTP.

Conceptualization, Writing - review & editing; Roberto Parra-Saldívar: Conceptualization, Funding Acquisition, Supervision.

Data availability

All data correspond to this work has been given and discussed appropriately. No additional or linked data is available.

Declaration of Competing Interest

Authors declare no conflict of interest in any capacity, including financial and competing.

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