MICROALGAE POTENTIAL IN THE CAPTURE OF CO_2 EMISSION

Francesca Frongia
Department of Life Sciences, University of Modena and Reggio Emilia,
via G. Campi 103, 41125 - Modena, Italy
https://orcid.org/0000-0002-1218-6661

Laura Arru
Department of Life Sciences, University of Modena and Reggio Emilia
via G. Amendola 2, 42122 - Reggio Emilia, Italy
https://orcid.org/0000-0002-1807-1689

Maria Rita Cramarossa
Department of Life Sciences, University of Modena and Reggio Emilia
via G. Campi 103, 41125 - Modena, Italy
https://orcid.org/0000-0002-6066-7355

Luca Forti*
Department of Life Sciences, University of Modena and Reggio Emilia
via G. Campi 103, 41125 - Modena, Italy, luca.forti@unimore.it
https://orcid.org/0000-0002-5662-7756

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Abstract

In a perspective projected to reduce the atmospheric concentration of greenhouse gases, in which carbon dioxide is the master, the use of microalgae is an effective and decisive response. The review describes the bio circularity of the process of abatement of carbon dioxide through biofixation in algal biomass, highlighting the potential of its reuse in the production of high value-added products.

Keywords
Microalgae, CO_2 biofixation, circular bioeconomy

Introduction

Greenhouse effect and decarbonisation strategies

Earth's temperature is rising almost 0.15°- 0.20°C per decade since 1975, causing an increase of 1° C since 1880 [1,2]. Scientists believe that this trend cannot be explained uniquely by natural changes, but it has to consider the influence of other factors, first of all the effect of the anthropogenic emission of large quantities of greenhouse gases (GHGs). GHGs include CO_2, methane, nitrous oxide, hydrofluorocarbons, chlorofluorocarbons, etc. Considering that many GHGs can remain in the atmosphere for tens or hundreds of years, creating serious consequences even in the long term, the situation is even more critical. In order to counteract this trend, and to protect the environment, many Countries pledged to enter into agreements such as the Kyoto Protocol (1979) and the Paris Climate Agreement (2015). Among the GHGs, CO_2 is considered to have the greatest negative impact on global warming. The rise of atmospheric CO_2 concentration has been about 2 ppm/year in the last ten years, and in 2019 was almost 40% higher (399 ppm) than that measured during the Industrial Revolution (280 ppm) [3,4]. Since CO_2 is one of those gases with exceptional persistence in the atmosphere (even if also non-CO_2 greenhouse gases could have a negative role as well) [5], transported by the wind and spreading all over the world, it can be responsible for global warming virtually irreversible for more than 1,000 years. Although still controversial and debated [6,7], contribution of fossil fuels-burning power plants seems to be about 40% of the total CO_2 global emission [8], to which burning of fossil fuels for transport must be added [9]. In heavy industries, CO_2 emissions are a by-product produced through chemical reactions that do not involve combustion, but also CO_2 emissions indirectly produced by electricity generation must be taken into account [9]. Some predictive studies show how the failure to reduce the GHGs emissions will affect the

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atmospheric temperature in coastal areas by 2°C by 2050 and by 4°C by 2100, while in inland areas the temperature will increase by 4°C by 2050 and by 7°C by 2100.

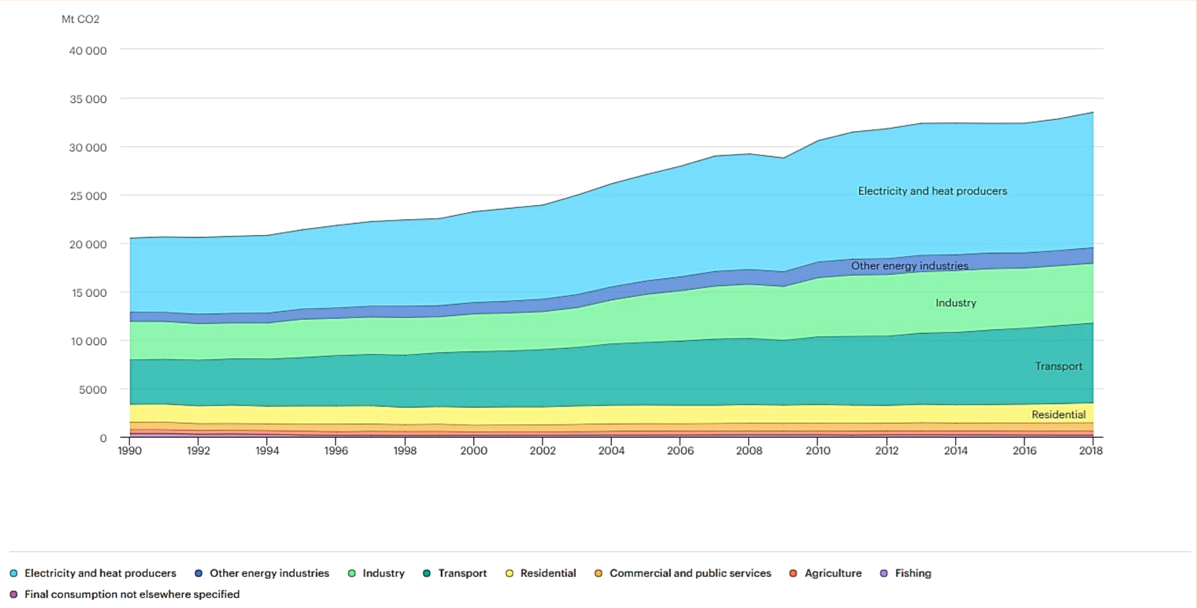

Fig.1. CO_2 emissions by sector. *Source: https://www.iea.org/articles/global-CO2-emissions-in-2019*

Although the combustion of fossil fuels is currently the cheapest form of energy production, it is one of the main factors contributing to CO_2 emissions into the atmosphere [10].
Several studies focus on finding solutions both to reduce atmospheric CO_2 pollution (by removing it from atmosphere or by reducing industrial emission) and to give alternatives to fossil fuels [10,11].

The main chemical processes to reduce CO2 presence in the atmosphere capture are absorption by amino solvents to treat industrial air flows [11,12] and adsorption of CO_2 molecules to a solid phase [13].
However, both chemical processes are economically disadvantageous, due to the energy consumption for solvent regeneration in the first case, and for separation of pollutants from adsorbents in the second one [13].

Microalgae CO_2 capture and utilization

In recent years, the concept of circular bioeconomy has emerged, focusing on the sustainable valorisation and transformation of biomass in production chains converting agro-industrial wastes into high added value products and use of renewable resources into products with a high added value [14]. The use of versatile and environmentally friendly photosynthetic organisms such as microalgae represents a promising approach in the development of such closed loop systems [15,16].
In Nature, Microalgae play a key role in the mitigation of environmental carbon and in bioremediation thanks to their high photosynthetic efficiency -about 40% more than terrestrial plants-, and to the significant sequestration of CO_2: about 1 kg of microalgae consumes 1.83 kg of CO_2 and represents 40% of the global CO_2 sequestration [16].
Microalgae has been studied not only to reduce CO_2 from the atmosphere or from flue gas emissions [17], but also to be applied in wastewater treatments [18] to generally lower pollutants and converting them into organic biomass rich in lipids, proteins, and other high value-added compounds [19] for energetic applications (biodiesel, biogas), food (human and animal feed), pharmaceuticals and cosmetics production [20].
Optimisation of carbon fixation efficiency by microalgae should take into account many variables.

It should be considered the use of the most suitable strain in relation with the different mediums to be treated, adjusting operating conditions as physicochemical and hydrodynamic parameters [8]. Good characteristics are tolerance to high CO_2 concentrations, high temperatures, and presence of toxic compounds such as NO_x, SO_x, hydrogen sulfide. For this reason the search for appropriate microalgae strain is one of the main concerns regarding the improvement of CO_2 capture processes [21]. Several microalgae such as *Chlorella spp.*, *Scenedesmus spp.*, *Chlorococcum spp.*, *Nannochloropsis* spp. have shown good ability to capture the CO_2 present in effluents similar to those emitted by industrial activities [22–25].

The supply of nutrients plays a fundamental role in the regulation of key metabolic processes related to both CO_2 fixation and biomass synthesis. Nutrients for microalgae cultivation include carbon, nitrogen, phosphorus, magnesium, sulfur and trace element [26].

When microalgae are grown in autotrophy, light is crucial for photosynthetic activity, being the energy source. The growth of microalgae and the fixation of CO_2 depend on both the light-dark cycle and the intensity of the light, but this is not a universal rule. CO_2 fixation by *Aphanothece microscopica Nägeli* and by *Nannochloropsis sp*. achieves approximately 100% efficiency with continuous illumination of the culture [27]. There is also evidence that shorter lighting periods lead to a reduction in biomass production and carbon dioxide fixation [27].

Another crucial parameter to enhance both CO_2 capture and cell growth is temperature. The solubility of CO_2 depends on temperature and is reduced at high temperatures. Besides, also the affinity of RuBisCO (the key enzyme for CO_2 fixation) for CO_2 decreases as the temperature increases. In any case, the effect of temperature on the reaction metabolic rate depends on the strain being considered [28].

The value for pH determines the form in which dissolved inorganic carbon (DIC) exists in water. CO_2, HCO_3^-, CO_3^{2-} and H_2CO_3, can all be found in water, but only CO_2 and HCO_3^- can be used by microalgal cells. The acidic pH favors the formation of H_2CO_3, whilst the alkaline one allows the assimilation of NO_3^- and HCO_3^-. It is generally preferred to cultivate microalgae in alkaline conditions due to the positive effect on CO_2 solubilization [29].

Microalgae cultivation systems for CO_2 capture

Microalgae can be produced either in open (outdoor) or closed systems (photobioreactor).

Open systems for microalgae growth are the cheapest, but they are also the most prone to the effects of external factors and contamination. Closed cultivation systems, also known as photobioreactors (PBR), despite being more expensive, allow the strict control of cultivation parameters, favoring the most suitable conditions for the growth of microalgae [30].

Typical configurations for CO_2 capture systems are tubular or flat PBRs.

Tubular PBRs are commonly used for CO_2 capture due to good scalability and low contamination risk. They are divided into horizontal and vertical tubular reactors [30]. The main advantages of horizontal PBRs are the large surface exposed to light and the relatively low CO_2 losses [31]; on the other hand, an important disadvantage is the accumulation of oxygen in the culture medium, that can lead to a decrease in biomass production and CO_2 uptake [29]. Vertical PBRs, on the other hand, are advantageous for their high mass transfer and good mixing, which has made them suitable systems for biomass production and CO_2 sequestration; however, they have a small illumination area, which can induce a decrease in the growth rate [32].

Another configuration commonly used for CO_2 capture with microalgae are flat plate PBRs. An important advantage is the short light path and high illumination area. An important drawback is the low mixing and high shear stress [32].

Effect of flue gas compounds on microalgae

In order to apply the biofixation of microalgae to industrial power plants or fuel gases it is necessary to understand the influence of combustion gas compounds on microalgae (Tab. 1).

In fact, in addition to the CO_2 contained in about 10/15% in coal-fired power plants and 5/6% in natural gas-fired power plants, nitric oxide (NO) and nitrogen dioxide (NO_2) are present in flue gases, as well as SO_x [33].

In combustion gases the level of NO_x emission varies from 90/95% of NO and 5/10% of NO_2. If the NO concentration is very low, it is transformed into NO_2 and absorbed as a nitrogen source. However, the increase in NO concentration may lead to a decrease in the growth rate for some microalgal species [8].

SO_x are produced by burning hydrogen sulfide, sulfur, or organosulfur compounds. It is well known that the presence of SO_2 strongly inhibits microalgae growth. Inhibitory effects of SO_2 on microalgae growth can be attributed to increased acidity, which leads to cell death. A pH control in the growth medium would maintain algal growth unvarying in the presence of SO_2 [8].

Concerning the interaction between microalgae and other compounds as unburnt hydrocarbons, O_2, N_2, C_xH_x, H_2O, CO, aerosols, heavy metals, and particulate matter, they have yet to be studied in detail.

Table. 1. Inhibition effects of microalgae species cultivated using flue gas with SO_x and NO_x compounds. *Source: [4]*

Microalgal species	CO_2% (v/v)	NO_x (ppm)	SO_x (ppm)	Source	Inhibitory effect	Cultivation system	References
Nannochloropsis limnetica	10	-	25	Real flue gas from rice husk emission	Inhibited	Bubble column	[34]
	3	-	11	Real flue gas from rice husk emission	Inhibited	Bubble column	[34]
Chlorella sp.	8-10	38	3.8	Real flue gas from co-generator units	No inhibition	Bubble column	[35]
	6-8	37	-	Real flue gas from combustion of natural gas from boiler	No inhibition	Open thin layer PBR	[36]
	23	78	87	Real flue gas from coke oven of steel plant	No inhibition	Double set PBR	[37]
Chlorella sp. MTF-15 6–8	25	70-80	80-90	Real flue gas from coke oven of steel plant	Slight inhibition	Column-type glass-fabricated PBR	[22]
	26	8-10	15-20	Real flue gas from coke oven of steel plant	Slight inhibition	Column-type glass-fabricated PBR	[22]
	24	25-30	15-20	Real flue gas from coke oven of steel plant	Slight inhibition	Column-type glass-fabricated PBR	[22]
Scenedesmus sp.	18	150	200	Real flue gas from combustion chamber of coke oven	No inhibition	Airlift	[38]
Mixed culture of Scenedesmus sp., Chlorella sp., Nitzschia sp., Chlamydomonas sp., Oocystis sp. & Protoderma sp.	7.5	77	-	Real flue gas from combustion of natural gas in manure-drying motors	No inhibition	High-rate algal pond	[39]

Applications of CO_2 capture and utilization by microalgae

To date, there are few examples of commercial applications of microalgae for the capture of CO_2 in a biorefinery concept, due to the high process costs [40].

Here are some examples of successful pilot scale applications.

The first company in the world to use the exhaust gases of a power plant for seaweed farming was Seambiotic, in Israel. The first company in the world to use the exhaust gases of a power plant for seaweed farming was Seambiotic, in Israel. In 2006, this company, in collaboration with a coal-burning power plant in the city of

Ashkelon, developed a pilot plant with a pond area of 1000 m^2, to test algae growth using CO_2 from flue gases. The plant produced around 7 tons of biomass per year from flue gases containing 12% vol CO_2. Subsequently, the Hearol project, by Seambiotic, Yantai Hairong Electricity Technology and Penglai Weiyuan Science & Trading Ltd was developed, with the aim of using the exhaust gases generated by the Penglai coal-fired power plant to grow microalgae on a commercial scale [21].

In Germany, RWE has started a project in which combustion gases from the Niederaussem power plant are fed into an algae plant near the plant to convert CO_2 into biomass. The plant has been operational since 2008 on an area of 600 square meters and supplies about 6000 kg of algal biomass using about 12000 kg of CO_2 per year [41].

At the University of Kentucky in the United States, researchers cultivated *Scenedesmus acutus* in an 18,000-liter pilot-scale PBR system using exhaust gas derived from Duke Energy's East Bend Power Plant, Kentucky. The exhaust gas was initially pre-treated to reduce SO_x and NO_x and then pumped into the culture systems. The mean growth rate recorded during the study was 32.9 g m^{-2} d^{-1} [42].

The Daqi project in China is capable of capturing 110 tons of CO_2 with microalgae and producing respectively 20 tons of biodiesel and 5 tons of protein per year [21].

Eni, an Italian multinational active in fuel and natural gas sectors, started in 2019 the experimental plant for the CO_2 biofixation from microalgae thanks to the aid of artificial led light. The process, through CO_2 biofixation by microalgae, allow to enhance CO_2 as a raw material and to transform it in high value products such as algal flour for food and nutraceutical markets or biooil, which can sequentially be used as feedstock in biorefineries. The pilot plant consisting of 4 PBRs is integrated with renewable energy sources, and has achieved daily productivity data of biomass that could lead to 1 hectare plant producing 500 tons of biomass per hectare per year, trapping about 1000 tons of CO_2 [43].

Between 2011 and 2013, the Green Mission project (a collaboration between the State of Brandenburg, the European Union and Vattenfall) followed by the Green Vision project, tested an algal farm facility using the combustion gas obtained from the Senftenberg power plant (Brandenburg). The facility is one of the largest closed algal cultivation systems globally with a volume of 48000 L, with an increased biomass productivity using raw combustion gas [21].

Environmental and economic impacts aspects of CO_2 capture and utilization by microalgae

Microalgae are receiving increasing attention due to their potential application to the capture and use of CO_2 in the renewable energy sector. The use of microalgae has several advantages over the use of other plant raw materials, including a high photosynthetic conversion, a high capacity to produce different raw materials for biofuels, a high environmental bioremediation capacity (CO_2 fixation from atmosphere or from combustion gases, water purification) and the non-competitiveness for the use of land for food crops. Furthermore, net CO_2 emissions are assumed to be essentially zero if the CO_2 released from the biofuel from microalgae can be recycled and reused for microalgae cultivation. Consequently, these advantages and potential make microalgae suitable for solving CO_2 and energy reduction problems [33].

CO_2 capture through a biorefinery approach with microalgae cultivation is economically feasible, as waste from power plants or other industrial plants is reused [44] and residual microalgae biomass, rich in proteins and carbohydrates, can be used as a carbon source for the production of bioelectricity, biohydrogen and also fatty acids and other molecules, which can in turn be used to produce bioplastics [45].

A very promising algae for capturing CO_2 from flue gases is chlorella. Studies have shown that Chlorella could grow in an atmosphere containing up to 40% (v / v) CO_2, with a CO_2 fixation rate between 0.73 and 2.22 g/L/day. [4,45].

A very important aspect concerns the fact that the NOx and SOx compounds present in the fed CO2 stream do not affect the production of *Chlorella* biomass. [4,46]. In fact, some studies reported how these pollutants are metabolized at the cellular level by microalgae in culture [22,47]. Some microalgal species could therefore be potentially useful for bioremediation of CO_2, but also of other greenhouse gases [47].

Therefore, the main purpose is the conversion of CO_2 into different products, thus closing the carbon cycle and contributing to the bioeconomy of the process [48].

The EU emission trading scheme (ETS) is a milestone of EU policy to tackle climate change and a key tool for cost-effectively reducing greenhouse gas emissions. It is the world's leading CO_2 market and continues to be the largest. The ETS is a free trade program where, one the state has set the limit for the environmental load of carbon dioxide that can be emitted distributes to companies an amount of exchangeable certificates capable of covering the fixed quantity. Those who are unable to cover their emissions incur the payment of financial penalties. The most important parameter of all is therefore the method of assignment of certificates. In order to achieve climate neutrality in the EU by 2050, including the interim target of a net greenhouse gas emission reduction of at least 55% by 2030, the Commission proposes to review and possibly extend the scope of the EU ETS system.

The main impact produced by the ETS is represented by the cost that companies will have to face to obtain the necessary permits to cover their emissions, so being the cost of innovative technologies for the reduction of CO_2 emissions presumably lower than the expected cost of purchasing new certificates on the market, companies will feel encouraged to adopt new technologies.

The possibility of acquiring a valid and efficient technological innovation that allows to reduce, at least in part, the polluting CO_2 emissions by channelling the latter into photobioreactors to produce biomass, must make us reflect and think about a whole series of other important benefits that can be drawn from the use of this technology. Firstly, part of the cost currently incurred only for the "virtual" compensation of CO_2, which continues to flow into the atmosphere, would be invested. On the other hand, the biosynthesis operated by microalgae intervenes in this process by sequestering and transforming inorganic carbon (CO_2) into organic carbon and returning molecular oxygen to the environment.

Impact

Microalgae are capable to convert CO_2 from the atmosphere and from flue gas, leading to a reduction of GHGs emissions. Thanks to this, the greenhouse effect will be reduced, and therefore also global warming, achieving a healthier environment. Worldwide emissions of CO_2, about 40 Gt per year, are too high compared to about 14000 tons of microalgae biomass commercialized (about 27000 tons of CO_2 biofixed). This incredibly low contribution highlights the need to boost productivity and improve existing technologies in order to generate more microalgal biomass capable of capturing more CO_2 [29]. One of the most important aspects related to the capture of CO_2 from microalgae is the reuse of biofixed biomass for energy production, considering the need to meet global energy demand. Moreover, CO_2 biofixation using microalgae is combined with other processes like wastewater treatment: this is advantageous to offer more economical feasibility and environmentally sustainability.

The transition from pilot to industrial scale is difficult to apply as microalgal cells are exposed to hostile circumstances, resulting in a reduction in CO_2 biofixation and product yield. Therefore, it is necessary to integrate the use of promising algal strains, optimized process parameters, targeted cultivation systems, to ensure economic and environmental feasibility on a large scale.

Conflict of interest

There are no conflicts to declare.

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