



# Perspective Microalgal Carbon Dioxide (CO<sub>2</sub>) Capture and Utilization from the European Union Perspective

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Abstract: The increasing concentration of anthropogenic  $CO_2$  in the atmosphere is causing a global environmental crisis, forcing significant reductions in emissions. Among the existing  $CO_2$  capture technologies, microalgae-guided sequestration is seen as one of the more promising and sustainable solutions. The present review article compares  $CO_2$  emissions in the EU with other global economies, and outlines EU's climate policy together with current and proposed EU climate regulations. Furthermore, it summarizes the current state of knowledge on controlled microalgal cultures, indicates the importance of  $CO_2$  phycoremediation methods, and assesses the importance of microalgae-based systems for long-term storage and utilization of  $CO_2$ . It also outlines how far microalgae technologies within the EU have developed on the quantitative and technological levels, together with prospects for future development. The literature overview has shown that large-scale take-up of technological solutions for the production and use of microalgal biomass is hampered by economic, technological, and legal barriers. Unsuitable climate conditions are an additional impediment, forcing operators to implement technologies that maintain appropriate temperature and lighting conditions in photobioreactors, considerably driving up the associated investment and operational costs.

**Keywords:** carbon dioxide emission; CO<sub>2</sub> capture; biosequestration; microalgae; long-term utilization; phycoremediation; fit for 55

## 1. Introduction

Extensive carbon dioxide  $(CO_2)$  emissions into the atmosphere have created an environmental crisis and are considered the main driver of global warming [1]. Almost 65% of greenhouse gas (GHG) emissions are accounted to  $CO_2$ . Addressing the impacts of global warming has become a pressing concern for both economic systems and environmental/energy regulations in recent years [2]. Climate and ecological disasters have posed threats to humanity and thus forced decision-makers, politicians, and companies to significantly reduce anthropogenic GHG emissions into the atmosphere, with particular focus on  $CO_2$ . European Union (EU) nations have taken decisive and unwavering steps, consistently executing robust plans towards becoming carbon neutral in 2050 [3].

It is widely acknowledged that GHGs play a positive role by stabilizing temperature at an equilibrium beneficial for natural ecosystems. However, increasing net  $CO_2$  in the air by long-term intensive combustion of fossil fuels causes global temperatures to rise uncontrollably and to an excessive degree. Climate change is currently treated as a key issue to be tackled, as it is considered a global threat to civilization [4]. Numerous papers have shown that increased levels of atmospheric  $CO_2$  are detrimental to economic and agricultural development, water regimes, tourism, food production, and other branches of the economy [5].

Given the above, new technologies need to be developed to reduce  $CO_2$  emissions into the atmosphere. This can be achieved by utilizing conventional methods based on



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). low-emission or zero-emission technologies for fuel and energy production and use [6]. Another avenue is to develop and deploy effective methods of  $CO_2$  sequestration. This refers to all processes designed for the purpose of capture, separation, transport and long-term storage of  $CO_2$  in a suitable and safe location. Depending on the stage of the process, sequestration methods can be divided into direct and indirect ones. Direct sequestration aims to capture  $CO_2$  before it is released into the atmosphere, then transport it to where it can be stored or re-used. Indirect sequestration serves to reduce  $CO_2$  emission, i.e., binding of gases previously released into the atmosphere.  $CO_2$ -absorbing plants can be used for this purpose, for example, by phycoremediation techniques. Atmospheric  $CO_2$  can also be fixed in the soil [7]

Mineral sequestration, referred to as mineral carbonation, is one of the most extensively explored direct methods. The technology involves the production of stable carbonate compounds by reacting CO<sub>2</sub> with artificially produced substances, naturally occurring substances in the environment, or other compounds (including waste) [8]. Solutions are sought to improve the performance and cost-effectiveness of mineral carbonation [9]. Despite its many advantages—such as safe and long-term binding of CO<sub>2</sub>, as well as the sorption capacity of the materials—its potential for wide exploitation is hampered by the high operation and investment costs, the costs of acquiring and storing the minerals, the limited availability of effective adsorbents, and the technological complexity of the process. One of the most well-explored methods of storing  $CO_2$  is sequestration in geological formations, which has attracted attention due to its capacity to store large amounts of gas and the gas accumulation time [10]. This concept calls for storing CO<sub>2</sub> in deep permeable formations covered by impermeable layers. The underground sites most commonly cited as suitable for storing  $CO_2$  are: deep aquifers, productive or depleted oil/gas reservoirs, and unused coal deposits. Other commercially- and technologically-viable approaches to capturing and removing  $CO_2$  from flue gas include physical processes (adsorption, membrane separation), chemical processes (adsorption and chemical absorption), and biological processes (forest plantation, ocean fertilization and using photosynthesizing microorganisms) [11]. A basic division of the methods used for binding  $CO_2$  is presented in Figure 1.



Figure 1. Classification of CO<sub>2</sub> capture and sequestration methods.

Out of the myriad available options, microalgae-mediated biosequestration is considered to be a promising solution that could help reduce atmospheric  $CO_2$  emissions. The particular properties of microalgae—specifically, their extremely efficient utilization of solar energy and rapid growth of biomass—mean that microalgal biomass production systems offer considerable technological performance. Figure 2 presents a diagram of the biochemical conversion routes that transport  $CO_2$  into microalgal biomass structures [12]. Bioreactors can harness anthropogenic waste produced by industrial and domestic sources [13]. This enables commercial systems of microalgae biomass production to be established on land unsuitable for agricultural use, near heating/cogeneration plants, sewage treatment plants and other industrial facilities that produce carbon dioxide and biogenic compounds.



Figure 2. Mechanism of microalgal CO<sub>2</sub> sequestration via photosynthesis [12].

Successful implementation of methods for the capture and utilization of  $CO_2$  requires not only that productive and cost-effective technologies be developed, but also that international agreements and pursuant emission limits/regulations be put in place [14]. The EU countries are currently undertaking bold and forward-looking actions in this respect, including with regard to circular economy, the Fit for 55 package, and the Green Deal [15]. The European Commission (the EC) has put forward a set of legislative proposals designed to align EU legislation, with its new greenhouse gas emission targets, with emissions to be reduced by at least 55% by 2030 (relative to 1990 levels). This package of proposals forms part of the European Green Deal, which aims to make Europe the first carbon-neutral continent by 2050. It should also be noted that the Climate Law adopted by the European Parliament in April 2021 requires that objectives be defined for 2040. This means that the Fit for 55 package is only one step towards neutrality, and that new regulatory packages can be expected in the second half of the decade [16].

The aim of this paper is to present and analyze current knowledge on the feasibility of technologies for  $CO_2$  capture and biosequestration using microalgae biomass. A literature review was conducted to compare  $CO_2$  emission levels of EU countries with other global economies, to present current and proposed  $CO_2$  regulations in the EU, to present an overview of technologies for producing microalgae biomass under controlled conditions, to define their applicability for reducing emissions in the EU, to discuss the importance of

 $CO_2$  phycoremediation methods, and to assess the importance of microalgae-based systems for long-term storage and utilization of  $CO_2$ . The paper also identifies existing limitations and barriers to the successful implementation of microalgal technologies across the EU countries.

#### 2. Global and EU Trends in CO<sub>2</sub> Emissions

According to analyses and statistics from the International Energy Agency, energy demand fell by 4% in 2020, whereas  $CO_2$  emissions (which are tied to energy production) decreased by an estimated 5.8% [17]. Though this represents the largest percentage reduction since World War II, it should be considered a short-term anomaly in the long-standing upward trend in emissions [18]. The decline is directly attributable to the economic slowdown observed in many sectors, caused by restrictions imposed in response to the SARS-CoV-2 pandemic. The most pronounced decrease was observed in developed countries (up to 10%), whereas developing countries showed less of a reduction (approx. 4%). China, the world's largest emitter, was the only country to increase its  $CO_2$  output [19]. Global fossil  $CO_2$  emissions are given in Figure 3a [20], whereas  $CO_2$  emission levels by source of fuel are presented in Figure 3b [20].



Figure 3. Emissions of  $CO_2$  from fossil fuels from 1960 to 2021: (a) global, (b) by source of fuel [20].

 $CO_2$  emissions by China were 4% larger in 2021 compared to 2020 and 5.5% larger than in 2019, reaching 11.1 billion tons of  $CO_2$  released. This translates to a 31% share in global emissions [20]. In turn, the USA produced 5.1 billion tons  $CO_2$  in 2021, which accounts for 14% of global emissions, whereas India released 2.7 billion tons  $CO_2$  in 2021—12.6% higher than in 2020, but 4.4% lower than in 2019, which makes it account for approx. 7% of the global emissions [20].

Coal and gas consumption in the global economy is rapidly growing as a result of stimulus packages driving consumption, as well as the shift from spending on services in favor of industrial goods. The SARS-CoV-2 pandemic and the global lockdown caused societies to stop their spending on leisure and tourism sectors, instead focusing on material goods [21]. If the global consumption of coal keeps rising at its current, rapid pace, the resultant  $CO_2$  emissions will most likely exceed their 2014 peak. Recent oil consumption was relatively low, mainly due to the ongoing restrictions on travels [22]. However,  $CO_2$  emissions from oil operations are expected to rise by 4.4% this year; though, taking into account the earlier decline in 2020, they will still be 6% lower than the 2019 level [20].

Emissions in the 27 EU Member States were 7.6% higher than those in 2020, but 4.2% lower than in 2019, at 2.8 billion tons  $CO_2$ . As such, the EU's share in global emissions is currently 7%. The whole continent of Europe produced 5571.28 Mt of fossil fuel  $CO_2$ ,

which accounts for 14.65% of global emissions [23]. Out of that, the 27 European Union countries and the United Kingdom produced 3303.97 Mt (8.69% global share). The largest emitters are: Russia (1792 Mt), Germany (702 Mt), the United Kingdom (364 Mt), Italy and San Marino (331 Mt), Poland (317 Mt), France and Monaco (314 Mt), Spain and Andorra (259 Mt), and Ukraine (196 Mt). Eurostat estimates indicate that CO<sub>2</sub> emissions fell across all of the Member States in 2020, with the average rate of decline being approx. 10%. The most significant drop was noted for Greece (-18.7%), followed by Estonia (-18.1%), Luxembourg (-17.9%), Spain (-16.2%), and Denmark (-14.8%). Conversely, the reduction was the least pronounced for Malta (-1.0%), Hungary (-1.7%) as well as Ireland and Lithuania (-2.6% each) [24]. Nevertheless, these reductions were only temporary and stemmed from the economic downturn caused by the SARS-CoV-2 pandemic. Germany's  $CO_2$  output rebounded in 2021, rising by 33 billion tons compared to 2020 and reaching 772 billion tons. The 2021 increase in  $CO_2$  was in large part driven by the economic recovery, which has radically pushed up the prices of various energy carriers [25]. The share of renewables was also relatively low, mainly due to the relatively windless weather. As such, the fossil fuel share in electricity production was larger than in 2020. These trends favored lignite/brown coal in particular (which has tremendous environmental impact), even despite the higher prices of emission allowances bought by power plant operators in 2021. The levels of emissions for fossil fuel combustion and cement production in the EU are presented in Figure 4a [20]. There has been a clear long-term pattern of reducing the consumption of oil and coal in favor of natural gas.



**Figure 4.** Emissions of CO<sub>2</sub> from cement and fossil fuels from 1960 to 2021 (**a**) in the EU, (**b**) per capita CO<sub>2</sub> by countries [20].

Any comprehensive and objective assessment of CO<sub>2</sub> emissions must take into account their per capita levels. The United States is the leader in this category, despite the downward trend in the last 20 years. China has recently caught up to and overtaken the EU (Figure 4b) [20]. India's per capita emissions are still only a fraction of those generated by industrialized countries [26].

#### 3. Current and Proposed EU Regulations

Under the Kyoto Protocol on climate change, which was concluded in December 1997, the European Union is committed to reduce its greenhouse gas emissions by 8% compared with the 1990 levels in the period 2008 to 2012. For the second commitment period of the Kyoto Protocol (2013 to 2020), the emissions are to be cut even further—a 20% reduction by 2020 (relative to 1990 levels). In the fourth phase of the EU ETS system (2021 to 2030), the EU intends to cut emissions by no less than 40% by 2030, in accordance with the 2015

Paris Agreement on Climate Change [27]. To that end, EU has set up a scheme for trading greenhouse gas emission allowances. Each emission allowance equals 1 ton of  $CO_2$  or  $CO_2$  equivalent within a given period [28].

One of the fundamental legal acts forming the basis of the current EU CO<sub>2</sub> emission trading scheme is Directive 2003/87/EC of 13 October 2003, amending the earlier Directive 96/61/EC of 24 September 1996, concerning integrated pollution prevention and control [29]. The prevailing greenhouse gas emission trading scheme (EU ETS) is the first and largest international scheme, covering almost 11,000 power plants and factories in 28 EU Member States plus Iceland, Norway, and Liechtenstein. It also regulates emissions generated by the aviation sector. This legal act forms the basis of EU's climate change mitigation policy and aims to control CO<sub>2</sub> emissions in a cost-effective and economically-efficient manner. The limits are set for the total quantity of a given greenhouse gas that can be emitted by the factories, power plants and other facilities covered by the scheme [30]. The applicable limits are systematically reduced in order to reduce total CO<sub>2</sub> emissions. The scheme allows emission allowances to be traded in a way which ensures that the total amount of emissions from industrial plants and aviation operations does not exceed the limit, and which will pave the way for the most effective emission mitigation measures.

The EU's new climate package is called 'Fit for 55': delivering the EU's 2030 Climate Target on the way to climate neutrality. On 14 July 2021, the European Commission adopted a package of legislative proposals seeking to amend EU climate, energy, land use, transport and taxation policies to reduce net greenhouse gas emissions by no less than 55% by 2030—relative to 1990 levels [31]. Under the package, 57% of the allowances are to be sold on auctions from 2021 onward. At least half of the revenues collected by EU countries must be allocated towards climate-related objectives. Operators who failed to purchase sufficient allowances must pay penalties of EUR 100 per each ton of  $CO_2$  released. The package's horizontal objective is to make Europe the first carbon-neutral continent by 2050 and implement the European Green Deal. The drafts submitted by the Commission are intended to provide legislative tools to achieve the goals of European Climate Law and to push the transition of the economy and society towards a fair, green, and prosperous future [32].

The 'Fit for 55' package consists of 13 legislative proposals. Proposed changes to current EU regulations include: changing the European Union's Emissions Trading Scheme (EU ETS), reforming the LULUCF Regulation (Land Use, Land Use Change and Forestry), reviewing the Effort Sharing Regulation (ESR), amending the Renewable Energy Directive (RED), amending the Energy Efficiency Directive (EED), revising the Alternative Fuels Infrastructure Directive (AFID), amending the regulation on  $CO_2$  emission performance standards for cars and vans, and revising the Energy Taxation Directive [33]. Novel legislative proposals include: a new EU Forest Strategy, a Carbon Border Adjustment Mechanism (CBAM), a social instrument for climate action, ReFuelEU Aviation (regarding sustainable aviation fuels), and FuelEU Maritime (regarding a green approach to maritime space) [34]. The main principles, rules, and objectives of 'Fit for 55' are presented in Table 1.

There are also EU-wide requirements in respect of the BIO component share in the conventional fuel blend, which also aims to significantly reduce  $CO_2$  emissions. EU aims to boost the usage of renewable energy sources (RES) in the energy mix through its policy initiatives. Reports on ILUC (Indirect Land Use Change Impacts), ordered by the EC, raise doubts about the environmental sustainability of biofuels produced from grain, root/tuber, and oil crops [35]. As such, the usefulness of using food sources for biofuel production is being progressively scrutinized in discussions at the EU level. Thus, advanced (second- and third-generation) biofuels need to be used instead [36]. The reports list types of feedstocks used for biofuel production that are multiple-counted for the purposes of calculating biofuel energy content. Algae are first on that list. Thus, there is a real need to seek different sources of biomass for biofuels, ones which would be both commercially and environmentally viable.

Pricing	Targets	Rules	
New carbon border adjustment			
mechanism (CBAM)	Updated Energy Efficiency Directive	New infrastructure for alternative fuels	
Updated Energy Taxation Directive	Updated Renewable Energy Directive	Stricter CO <sub>2</sub> performance for cars and	
Stronger Emissions Trading System	Updated Land Use, Land Use Change	vans	
including aviation,	and Forestry Regulation	FuelEU: cleaner maritime fuels ReFuelEU:	
extending emissions trading to maritime,	Updated Effort Sharing Regulation	more sustainable aviation fuels	
road transport, and buildings			
	Support measures		

Table 1. Overview of the EC's 'Fit for 55' package.

Combating climate change through the use of funds and regulations to foster innovation, enhance utility, and alleviate the effects on vulnerable communities through the establishment of the Social Climate Fund and improved Modernisation and Innovation Fund.

## 4. Microalgae—Potential Use to Reduce CO<sub>2</sub> Emissions

Microalgae are single-celled microorganisms which turn solar radiation energy to chemical energy using photosynthesis [37]. Their biomass can contain numerous bioactive substances with high potential for both commercial and industrial use. Microalgae can produce a variety of cellular metabolites such as high quality proteins, lipids, carbohydrates, dyes, and vitamins for food/feed, cosmetics and alternative energy industries [38]. Microalgae employ a mechanism known as the carbon-concentrating mechanism (CCM) for  $CO_2$  assimilation, using a specialized organelle (the pyrenoid) to raise  $CO_2$  levels around thylakoid membranes [39]. The increased  $CO_2$  levels around thylakoid membranes increase the efficiency of carboxylation/oxygenation of ribulose 1,5-bisphosphate (Rubisco), a photosynthesizing enzyme that plays a major role in carbon assimilation/sequestration. Rubisco has a low CO<sub>2</sub> binding affinity, having evolved in CO<sub>2</sub>-rich and O<sub>2</sub>-poor environments. As such, the pyrenoid acts to maintain optimal conditions for increased CO<sub>2</sub> binding capacity [40]. So far, various cellular components involved in transporting and storing inorganic carbon have been identified. However, the energy supply pathways for microalgae to accumulate CO<sub>2</sub> against the thermodynamic gradient remain unknown. Research has shown that in *Chlamydomonas reinhardtii*, the interaction between cyclic electron flow and  $O_2$  photoreduction is crucial for the  $CO_2$  concentration mechanism to function [41]. The process is dependent on the PGRL1 protein and flavodiron. The authors suggest that luminal protons are used downstream of thylakoid bestrophin-like transporters, possibly for the conversion of bicarbonate to  $CO_2$ . In addition, electron flow from the chloroplast to the mitochondria was found to contribute to the energization of non-thylakoid inorganic carbon transporters, possibly by providing ATP [41]. Microalgae-harnessing systems are increasingly considered for applications in engineering and environmental protection, especially in terms of wastewater treatment, solid waste neutralization, flue gas (including CO<sub>2</sub>) reduction, and biofuel production technologies (Figure 5) [42]. Technologies based on the microalgae cultivation are considered to be applicable in environmental protection and engineering systems, as well as for the production of other economically valuable products, including fertilizers, feed additives, dietary supplements and energy carriers. The advantage of these microorganisms and the very wide application potential result from the high efficiency of photochemical processes, the rate of biomass production, genetic diversity and resistance to harsh environmental conditions in relation to typical terrestrial plants [43,44].

Research has extensively described microalgae-based technologies for flue gas treatment, pollutant degradation, and biofuel production. The microalgal biomass has been shown to be some of the most potent and environmentally friendly alternative energy sources. It offers a renewable source of bio-oil, methane and biohydrogen, the use of which can help reduce atmospheric CO<sub>2</sub> emissions [45]. Research suggests that the yield of bio-oil from microalgal cultures can surpass 19 m<sup>3</sup> oil/ha·year. By comparison, the corresponding values for other sources are:  $6.1 \text{ m}^3/\text{ha·year}$  for palm oil,  $4.3 \text{ m}^3/\text{ha·year}$  for sugar cane, 2.4 m<sup>3</sup>/ha·year for maize, and 0.5 m<sup>3</sup>/ha·year for soy [46]. The main perk of microalgae is their high photosynthetic efficiency, as they are able to convert 4% to 10% of light energy to chemical energy. By comparison, higher plants photosynthesize at 0.5–2.2% efficiency. Research has shown that microalgal cultures can produce 36 tons dry matter/ha·year, whereas soy yields only 2.6 tons grain/hectare· year (growing conditions being the same). Some microalgae strains can double their mass in a matter of hours, producing yields equivalent to 100 tons dry matter per hectare [47].



Figure 5. Technologies and avenues for application of microalgal biomass [42].

Another advantage of microalgal production systems is their potential to utilize waste, including sewage of various characteristics, leachates, semi-liquid waste, and gaseous emissions. Microalgae can take up nitrogen and phosphorus compounds. In mixotrophic cultures, they can also metabolize a portion of the organic load. Currently, microalgae-based waste treatment mechanisms are often integrated into systems intended to produce biofuels [48]. Such solutions are thought to be more feasible from the commercial and technological standpoint, while also being able to reduce CO<sub>2</sub> emissions from fossil fuels. Direct use of waste as a feedstock cuts the expenses of providing water and nutrients necessary for the algae to grow effectively [49]. Studies conducted to date demonstrate

that elevated levels of  $CO_2$  enhance microalgal growth and thus directly contribute to the elimination of other pollutants [50].

Eutrophicated and degraded water bodies used for phycoremediation may also serve as a reassuring source of microalgal biomass [51]. Obtaining microalgae from such reservoirs prompts to direct improvements in the quality of water. Controlled growth of microalgae in eutrophicated sea water directly lowers the biogenic compound levels in the water. It also reduces the probability of marine life loss and can be used as a form of revegetation to enhance the quality of water bodies [52]. Microalgae can be cultivated both in water acquisitioned from natural bodies (with high levels of biogenes), and in liquid waste and wastewater of varying compositions. This process not only leads to more efficient biomass productivity but can also bring positive environmental outcomes. Microalgal biomass can be grown without using pesticides, which significantly lowers the risk of secondary pollution [53].

The main barriers to rapid advancement of microalgae-based technologies lies in their associated investment and operation costs, technological complications related to the cultivation, thickening and separation of biomass, as well as the financial commitments required to convert biomass into value-added final products [54]. The investment and operating costs tied to microalgal cultivation are significantly higher (more than ten times higher in some cases) than those associated with obtaining lignocellulosic biomass [55]. As such, both commercial enterprises and research groups are working on increasing the cost-effectiveness of such systems as a priority. The absence of norms, standards, legislative measures, legal frameworks, and incentives (such as subsidies and tax credits) presents another obstacle to the broad use of microalgae production solutions for biofuel production [56].

Nevertheless, microalgae-based technologies are being systematically developed, and given the progress and optimization achieved in this regard, as well as the pressure caused by environmental challenges, global prospects are promising (Figure 6) [57]. Within the EU, there has also been a steady rise in the number of installations (both pilot- and full-scale) for the industrial production of microalgae (Figure 7) [58].



Figure 6. Global prospects for development of microalgae-based technologies [57].



Figure 7. Number of microalgal production plants in the EU in 2021 [58].

### 5. Microalgal CO<sub>2</sub> Sequestration—The Current State of Knowledge

Results of experiments on microalgae-mediated  $CO_2$  sequestration to date indicate that it can become an alternative and competitive technology to bolster current methods. It should be emphasized that the method harnesses biological systems, which require stable and reproducible conditions to thrive. With the large variety of anthropogenic  $CO_2$ sources, each microalgae-based system will have to be tailored to the given industrial installation [59]. The literature data indicate that the composition of the released gas is determined by multiple factors, including the fuel from which the waste gas was produced, and how the system is used [60]. The  $CO_2$  levels in the flue gas from combustion and other production processes (such as hydrocracking) fall within the wide range from 3 to 85% vol.

Microalgae-based biosequestration systems, known as photobioreactors (PBRs), have multiple limitations. Research has shown that  $CO_2$  biosequestration efficiency can be severely impacted if the input gas contains high levels of sulfur oxides/nitrogen oxides/dust, or if it is heated to a high degree. In addition to  $CO_2$ , hundreds of other chemicals have been identified in the gases which can be fed into PBRs, and it is still unknown how these substances affect the photosynthetic process and its efficiency. It is reasonable to assume that many of them will have negative, inhibitory or toxic effects on the growing microalgae. At low concentrations,  $NO_x$  can be metabolized by microalgae and do not inhibit their metabolic activity. On the other hand,  $SO_x$  are toxic to microalgae [61]. A study by Stewart and Hessami [62] has demonstrated that a 4000 m<sup>3</sup> open system was able to remove 22,000 Mg  $CO_2$ /year.  $NO_x$  were taken up by the microalgal biomass as nutrients for growth.  $SO_x$  in the input gas should be less than 60 ppm [62].

So far, attempts have also been made to verify the possibility of using microalgae technologies in the processes of nitrogen oxide removal from exhaust gases. About 95% of them are dominated by NO, and the rest are N<sub>2</sub>O, N<sub>2</sub>O<sub>3</sub>, NO<sub>2</sub>, NO<sub>3</sub>. The possibility of NO fixation by microalgae biomass is hindered by its low solubility in water, which is only 0.032 g/dm<sup>3</sup> at a pressure of 1 atm and a temperature of 25 °C [63]. Dissolution is prerequisite for using nitrogen oxides in the process of intensive growth of microalgae biomass. Nitrogen is used to build nucleic acids and proteins. Microalgae reduction of nitrogen oxides is a prospective method, but the research has never gone beyond the laboratory scale. It has been proven that NO at a concentration of about 300 ppm can be biologically converted to NO<sub>2</sub>. Chiu et al. [64] proved that the average NO removal

efficiency was 70% for *Chlorella* LEB-106, with a pollutant concentration of 100 ppm NO and 60 ppm SO<sub>2</sub>. SO<sub>2</sub> dissolves very well in water at a rate of 22.971 g/100 gH<sub>2</sub>O at 0 °C to 5.881 g/100 gH<sub>2</sub>O at 40 °C. It was found that introducing gases with SO<sub>2</sub> concentration above 60 ppm into the culture should be avoided [64]. It has also been proven that the use of culture with a biomass concentration of 0.5 g/dm<sup>3</sup> reduces the sulfur toxicity to *Chlorella* MTF-7 cells, which were tolerant to SO<sub>2</sub> concentration of up to 90 ppm [64]. It is also believed that microalgae resistant to low pH conditions tolerate higher concentrations of this gas in the environment. Though there has been a noted decrease in the SO<sub>x</sub> levels in flue gases in recent years (thanks to the use of effective desulfurization technologies), they are still high enough to reduce pH and carbonate levels in the growth medium. The toxic effects of these compounds are exacerbated under acid conditions [65]. High concentrations of SO<sub>2</sub> and CO<sub>2</sub> can lower pH and cause highly toxic substances to form in the medium. To alleviate this problem, systems are amended with alkalizing substances, including NaOH [66]. High concentrations of SO<sub>2</sub> can also damage photosynthetically-active pigments and proteins.

The performance of microalgae-mediated  $CO_2$  sequestration is also strongly linked to the temperature of the gas. Highly heated gas can cause breakdown of chlorophyll and inhibit  $CO_2$  bindings, as demonstrated for *Chlorella sorokiniana* [67]. Conversely, *Chlorella* MTF-7 has been shown to perform the best when exposed to gas at 30 °C. Increasing the temperature in the PBR to 40 °C led to significantly reduced microalgal biomass [64]. These optimal temperatures necessitate the use of cooling systems, as flue gas temperature can be as high as 450 °C.

The exact effect of increased CO<sub>2</sub> availability on microalgal biomass growth rates differs from species to species [68]. *Chlorella kessleri* has been shown to grow the fastest at 6% CO<sub>2</sub> in the PBR. Increasing CO<sub>2</sub> levels to 12% led to its lower population growth rates. On the other hand, the increase had no effect on *Scenedesmus obliquus* cultures, which are more tolerant [69]. The high solubility of CO<sub>2</sub> in aqueous solutions may lead to acidification of the medium and inhibition of the biochemical processes. *Chlorella* sp. KR-1 populations have been shown to grow well at CO<sub>2</sub> concentrations in the flue gas ranging between 10 and 70% vol. [70]. Similarly, Chiu et al. [71] demonstrated a direct link between CO<sub>2</sub> levels in the flue gas and biosequestration efficiency when using *Chlorella* sp. In their study, the CO<sub>2</sub> removal ranged between 16% and 58% across the variants [71]. Cheng et al. [72] tested the capacity of *Chlorella vulgaris* cultures to capture CO<sub>2</sub> from the air. The CO<sub>2</sub> capture efficiency was linked to CO<sub>2</sub> levels in the membrane-treated air. Integrating a membrane module with a PBR resulted in higher CO<sub>2</sub> removal compared with a conventional system–260 vs. 80 mg/dm<sup>3</sup>·h, respectively [72]. A comparison of CO<sub>2</sub> sequestration rates across the experiments conducted to date is presented in Table 2.

Table 2. Literature data on the efficiency of microalgae-mediated CO<sub>2</sub> sequestration.

Species	Scale	photobioreactor Type	Growth Medium	Dry Matter Levels	Gas Type	CO <sub>2</sub> (%)	CO <sub>2</sub> Removal (%)	Ref.
Chlorella sp.	Laboratory	PBR	Modified f/2 medium in artificial sea water	$8 \times 10^{5} \text{ cells} \\ \text{mL}^{-1}$ (low-density) or $8 \times 10^{6} \text{ cells} \\ \text{mL}^{-1}$ (high-density)	Air supplemented with CO <sub>2</sub>	2–15	16–58	[71]
Chlorella sorokiniana	Laboratory	Air-lift PBR	Modified TAP (-acetate) medium	-	Flue gas	15.6	4.1	[67]
Chlorella sp. MTF-7	Laboratory	PBR	Modified f/2 medium in artificial sea water	0.1 g/L	Flue gas	25	60	[71]

Species	Scale	photobioreactor Type	Growth Medium	Dry Matter Levels	Gas Type	CO <sub>2</sub> (%)	CO <sub>2</sub> Removal (%)	Ref.
Chlorella kessleri			D 1	$0.15  \mathrm{g/I}  (\mathrm{dm})$	Air	6	-	
Scenedesmus obliquus	Laboratory	PBR	medium	biomass basis)	with CO <sub>2</sub> from a cylinder	12	-	[69]
Chlorella sp. KR-1	Laboratory	Conical flasks	Modified M4N medium	0.1 g/L	Air supplemented with CO <sub>2</sub>	10–70	-	[70]
Chlorella vulgaris	Laboratory	Membrane- PBR	Mineral medium	$\begin{array}{c} 2\times 10^7 \text{ cells} \\ mL^{-1} \end{array}$	Air supplemented with CO <sub>2</sub>	1	70	[72]
Chlorella vulgaris	Laboratory and large-scale	IMC-CO <sub>2</sub> PBR	Synthetic medium	100 g DM/L	Flue gas	25	45	[73]
Scenedesmus obliquus WUST4	Pilot scale	Air-lift PBR	Modified soil extract medium (SE medium)	OD685 = 2.0 (OD685 is the optical density at 685 nm, which is used to indicate the algal biomass density based on the turbidimetry)	Flue gas	18	64	[74]
Dunaliella sp.	Pilot scale	Air-lift PBR	-	-	Flue gas	-	$82.3 \pm 12.5$ (sunny days) $50.1 \pm 6.5$ (cloudy days)	[75]
Mixed biodiverse microalgal ( <i>Desmodesmus</i> spp. were identified as dominant microalgae)	Pilot scale	PBR	Bold Basal Medium and f/2 medium	0.1–0.4 g/L	Flue gas	11	-	[76]
Chlorella sp.	Pilot scale	PBR	Macronutrients (technical grade)–urea	-	Flue gas	6–8	10–50	[77]

Table 2. Cont.

Apart from the aforementioned primary determinants of effective  $CO_2$  biosequestration in microalgae-based systems, there are other major factors: PBR illumination, gas flow, and biomass concentration in the medium, as well as the methods used for stirring, for ensuring optimal gas retention in the biosequestration zone, and for maintaining interphase contact. The type of culture system, and the mechanism used to supply  $CO_2$ -rich gas, are factors cited as the most important [78].

## 6. Photobioreactors Used for CO<sub>2</sub> Biosequestration

A key factor, which in many cases determines the cost-effectiveness of microalgaebased systems, is the choice of culture method [79,80]. Algal biomass can be cultivated using a variety of methods, ranging from strictly monitored/controlled methods in technologically advanced designs to the less predictable methods based on open systems. The biomass can also be sourced from natural water bodies. The most commonly used systems for the production and extraction of microalgal biomass are presented in Figure 8.



**Figure 8.** Systems for production and extraction of microalgal biomass. (**A**) Raceway pond reactor (1—biomass extraction, 2—agitator blade, 3—nutrient dosing pump, 4—medium tank, 5—baffle). (**B**) Sack-type photobioreactor (1—medium tank, 2—nutrient dosing pump, 3—gas vent, 4—light source, 5—air supply and biomass extraction). (**C**) Flat plate photobioreactor (1—medium tank, 2—nutrient dosing pump, 3—air pump, 4—light source, 5—biomass extraction). (**D**) Tubular photobioreactor (1—medium tank, 2—nutrient dosing pump, 3—air pump, 4—light source, 5—biomass extraction, 6—gas outflow). (**E**) Biocoil-type photobioreactor (1—medium tank, 2—nutrient dosing pump, 3—biomass extraction, 4—recirculating pump, 5—light source, 6—air pump). (**F**) Installation for sourcing microalgal biomass from natural water bodies (1—intake pump, 2—settlement tank, 3

—series of drum filters, 4—separated algal biomass, 5—tank for biomass, 6—discharge). (**G**) Immobilized microalgae-based photobioreactor for CO<sub>2</sub> capture (1—photobioreactor housing, 2—support grid, 3—immobilized microalgal biomass, 4—capsule membrane, 5—fiber-optic cable, 6—light source, 7—CO<sub>2</sub> in, 8—gas pump, 9—CO<sub>2</sub> tank, 10—gas outlet, 11—nozzle, 12—growth medium dosing pump, 13—growth medium tank, 14—rinse pump, 15—settlement tank, 16—separation tank for excess algal biomass (including blue-green algae), 17—outlet, 18—valve, 19—discharge line, 20—liquid outlet, 21—in-capsule end of the optic-fiber cable, 22—line). (H) Diagram of a heterotrophic microalgal culture reactor (1—medium tank, 2—nutrient dosing pump, 3—gas outflow, 4—mechanical stirrer, 5—biomass extraction).

In systems that can be scaled up, using open cultures is often a way to reduce investment and operating costs [81] (Figure 8A). These usually consist of landlocked reservoirs with an area of 250 ha and depth of 0.5 m at most, either as circular ponds or raceway ponds stirred by agitator blades. These systems are handicapped by water losses through evaporation during operation, relatively low biomass growth, limited compatibility with certain algae species, and high vulnerability to infections, diseases, and parasites. These types of systems work well in areas with high sun exposure and unlimited access to water, which mostly relegates them to coastal areas. This technique is mainly used to grow *Spirulina* sp., *Chlorella* sp., and *Scenedesmus* sp. algae [82].

Sack systems of "large bags" are an example of a simple closed PBR design (Figure 8B), operating on a periodic or semi-continuous basis [83]. The main problem of this system is that the culturing process has to be conducted indoors and requires extensive additional lighting. Reactors of this type also fail to provide proper mixing, which limits biomass production. A variety of designs for flat plate reactors, as well as PBRs with vertical panels with separators, have been presented for growing different strains of algae [84] (Figure 8C).

Tubular reactors are usually built from glass or polycarbonate, with growth medium and gas being fed into the system using pumps or air lift systems [85] (Figure 8D). Such units can be horizontal, vertical, or inclined at an angle or conical. The biocoil reactor is a sub-type of the tubular photobioreactor (Figure 8E). It consists of a transparent hose wrapped around a core cylinder [86]. Microalgal biomass can also be obtained via phytoremediation (Figure 8F). This technology is designed to extract and separate microalgae from eutrophic/degraded natural water bodies, for their remediation and improvement of their trophic state. The efficiency of  $CO_2$  biosequestration is constrained by the comparatively low microalgal biomass levels in the cultivation medium. Therefore, there is an undeniable need to seek different solutions—ones which would be comparable in terms of performance and affordability [87]. One such alternative is to use PBRs that harness immobilized microalgae to CO<sub>2</sub> fixation from flue and exhaust gas (IMC-CO<sub>2</sub>PBR) (Figure 8G). This microalgae immobilization technology produces biomass yields close to 100 g DM/dm<sup>3</sup>, thus offering far better  $CO_2$  capture capacity than the conventional technologies [73]. It is also possible to grow and cultivate algal biomass in mixotrophic or heterotrophic systems, in which suitable carbon compounds are supplied to the bioreactors as nutrients for microalgae (Figure 8H). However, since the biomass is often grown without light or photosynthesis, these systems have limited applicability for CO<sub>2</sub> biosequestration. A comparison of microalgal culture systems is presented in Table 3.

Table 3. Comparison of technologies for microalgae-mediated CO<sub>2</sub> biosequestration.

Production System	Prospects	Limitation	
Open systems	Good for mass cultivation. Relatively economical after cultivation. Easier to construct, operate and clean up.	Requirement of large areas of land. Easily contaminated. Poor light utilization. Diffusion of CO <sub>2</sub> to the atmosphere. Evaporative losses. Limited to few strains of algae, cultures.	[88–90]

Tic bag photobioreactor

Production System Prospects		Limitation	Ref.
Flat panel photobioreactor	Low accumulation of dissolved oxygen and high concentration of sunlight per cm <sup>2</sup> . Modular design makes it easy to scale up production.	Algal biofilm formation. Strain-specific hydrodynamic stress issues. Temperature control issues.	[83,91,92]
Tubular photobioreactor	Good biomass productivities. Relatively inexpensive Suitable for outdoor.	Adverse pH and CO <sub>2</sub> gradients. High levels of dissolved oxygen. Fouling. Photoinhibition is very common (outdoor).	[93–95]
Tic bag photobioreactor	Good sterility.	Disposal of used plastic bags may present a	[96–98]

Table 3. Cont.

## 7. Methods of Feeding CO<sub>2</sub> to Microalgae Photobioreactors

Low cost.

To optimize production of microalgal biomass and thus improve the resultant  $CO_2$ capture capacity, the gas input to the growing microorganisms has to match their demand for gas. The well-known and widely used CO<sub>2</sub> delivery methods, based on diffusion and aeration, do not provide adequate performance [99]. Therefore, efficient and cost-effective methods for medium carbonization need to be developed to improve the performance of microalgae-based CO<sub>2</sub> biosequestration systems.

significant challenge at large scale operation.

One of such methods is to supply compressed air, pure  $CO_2$ , or exhaust/flue gas. The gaseous  $CO_2$  carrier is fed into the medium via a diffuser system at the bottom of the PBR. This method is, however, hampered by low performance, mainly due to the short retention time of gas bubbles in the culture medium, which limits the availability and transfer of  $CO_2$  to the microalgae biomass. It is characterized by significant losses of  $CO_2$  and high operation costs, due to the need to compress and supply the gas. It is estimated that up to 90% CO<sub>2</sub> fed into photobioreactors is not bioassimilated and is instead discharged from the system. When aeration is used to increase  $CO_2$  biosequestration rates, the size of the gas bubbles in the medium can be progressively reduced to bolster performance [100]. It has been demonstrated that microbubbles and nanobubbles promote CO<sub>2</sub> dissolution and its subsequent metabolization by microalgae. This stems from the increased surface-to-volume ratio of gas bubbles and retention time in the microbial activity zone. This method has been adopted from aerobic wastewater treatment technologies using activated sludge, designed with extensive oxidization of pollutants in mind. However, smaller bubble sizes produced by diffuser systems require higher energy expenditure, which drives up the cost of the process. In addition, this type of pressurized injection can generate huge shear forces, potentially damaging microalgae cell structures and thus inhibiting biological activity and  $CO_2$  biosequestration efficiency [101]. Shear forces, which are destructive to microalgae, can be mitigated or eliminated by using intermediate tanks and carbonization columns to which the microalgal biomass is transported for mixing with  $CO_2$ . Sparging or stirring systems have been found to accelerate the process. When carbonization columns are used, the culture medium mixed with microalgae biomass is poured in from above via sprinklers to ensure the countercurrent flow of medium and gas [102].

Membrane diffusers can be used to maintain the gas–liquid interface during  $CO_2$ supply and retention time in culture medium [103]. The membranes can be used with aeration or membrane contactors. The CO2 is compressed during membrane separation to generate gas bubbles 1–2 mm in size. When traditional diffuser systems are used, the gas bubble size ranges from 5 to 8 mm. The small pore sizes on the membranes necessitate high gas pressures. Membrane systems also require large surface areas and fine control of CO<sub>2</sub> pressure. In addition, they are sensitive to biological fouling during biofilm formation on the surface, which necessitates cleaning and periodic shutdowns [104].

Carbonization of the growth medium can be effected by using bicarbonate solutions. The inorganic carbon in the medium consists of  $CO_2$ ,  $HCO^{3-}$ , and  $CO_3^{2-}$ . Specific concentrations of these carbon species are a function of pH, alkalinity, salinity, and temperature. All photoautotrophic species of microalgae can directly utilize CO<sub>2</sub>. Many species are also able to take up and biochemically convert  $HCO^{3-}$  [105]. Microalgae-mediated  $CO_2$ sequestration systems thus depend on maintaining pH in the medium between 7 and 8, so that the inorganic carbon dissolved in the medium is kept in the form of  $CO_2$  and HCO<sup>3-</sup>. With the confirmed capacity of microalgae to take up HCO<sup>3-</sup>, carbonization of the culture medium can be boosted. The literature confirms that sodium carbonate can be used to grow microalgae [106]. High concentrations of bicarbonate salts have been shown to increase medium alkalinity, which inhibits microalgal population growth in the long-term and, in extreme cases, can be toxic to the culture, resulting in poorer CO2 biosequestration efficiency. This can be counteracted by using species resistant to and tolerant of extreme conditions, by slowly adapting the microalgae to increased medium alkalinity/salinity, and by supplementing the culture with dual streams of  $CO_2$  and  $HCO^{3-}$  gas. Bicarbonate solutions increase the alkalinity in the culture, which can enhance CO<sub>2</sub> dissociation in the medium. Although studies on bicarbonate salts have been promising and have, in many cases, shown improved microalgal biomass growth, this method is still commercially inferior to gaseous  $CO_2$  [107]. System performance as a function of the tested microalgae species and the mechanism of gas supply into the PBR is presented in Table 4.

Species	Supply Method	CO <sub>2</sub> Supply (%, <i>v/v</i> )	Scale	Biomass Produced (g/Ld)	CO <sub>2</sub> Removal Efficiency (%)	CO <sub>2</sub> Fixation Rate (g/Ld)	Ref.
Botryococcus braunii		0.03	1 L glass bottle	0.04	-	0.08	[108]
Botryococcus braunii		10	1 L glass bottle	0.02	$6.78\pm3.58$	0.03	[108]
Botryococcus braunii		20	1 L glass bottle	0.03	$3.73\pm0.74$	0.05	[108]
Chlorella pyrenoidosa		1	2 L flask	0.24	-	0.49	[109]
Chlorella pyrenoidosa	ng	10	1.8 L bubble column	0.14	95.1	0.25	[110]
Chlorella sorokiniana	Sparg	1	2 L flask	0.29	-	0.58	[109]
Chlorella vulgaris		0.03	1.5 L membrane bioreactor	0.05	-	0.09	[111]
Chlorella vulgaris		10	1.8 L bubble column	0.07	95.3	0.13	[110]
Scenedesmus dimorphus		10	1.8 L bubble column	0.12	94.6	0.22	[110]
Scenedesmus obliquus		10	1.8 L bubble column	0.15	94.7	0.27	[110]
Scenedesmus sp.		20	1 L glass bottle	0.13	$3.82 \pm 1.71$	0.23	[108]

Table 4. Biomass production and CO<sub>2</sub> sequestration rates as a function of pre-treated gas input method.

## 8. Microalgae as a Way of Capture and Utilization of CO<sub>2</sub> (CCU)

Utilization of captured  $CO_2$  removes the need for its storage and containment.  $CO_2$  capture and utilization/re-use is defined in terms of conversion into value-added, lower-/zero-emission products, including fuels, chemicals, carbon fibers, biomass, and building

materials. The CCU (carbon capture and utilization) should prove to be a useful tool in achieving zero/negative net emissions [112].

Microalgae-mediated CCU is a biotechnological process. In its first stage,  $CO_2$  is converted to biomass via photosynthesis [113]. The resultant biomass can be used to replace non-renewable fossil resources in the production of chemicals, fuels, bioplastics, diet supplements, cosmetics, pharmaceuticals, feedstuffs, and fertilizers.

Technologies for converting microalgae biomass to energy can be divided into two main groups: thermochemical and biochemical [114]. The production of biofuels from microalgae includes dark fermentation with methane [115] or hydrogen recovery [116], alcoholic fermentation to bioethanol [117], production of hydrogen from direct biophotolysis [118,119], production of biodiesel from storage lipids [120,121], pyrolysis gas [122] or syngas recovery [123] in thermal processes, and energy recovery from direct combustion of microalgae biomass [124]. In the energy transformation technologies of microalgae, apart from energy carriers, waste is generated, which is often used as fertilizer in agronomy [125].

Microalgae can be used as a potential tool for long-term CO<sub>2</sub> capture and utilization (Table 5)–for example, in the production of cement or bioplastics [126]. Production and utilization of biocarbon is another avenue of microalgae application–fixing carbon into soil provides long-term storage of CO<sub>2</sub> and serves to promote sustainable agriculture. Microalgae can also potentially be used as biostimulants to improve crop production, thereby reducing the need for chemical fertilizers. Microalgal biomass can also be used to produce bioplastics through CO<sub>2</sub> biosequestration [127]. Bioplastics are environmentally-friendly materials, as they do not increase the CO<sub>2</sub> pool and are quicker to biodegrade. Microalgae can contain high levels of polysaccharides, proteins or lipids, and may thus serve as an alternative to other bioplastics and replace traditional plastics and biodegradable materials (such as polylactic acid and polyhydroxyalkanoates). Biodegradable bioplastics reduce the pollutant load on oceans and reduce landfill areas, currently overfilled with non-degradable plastics. Using microalgae for cement production can serve as another method of long-term CO<sub>2</sub> capture. The process involves the precipitation of CaCO<sub>3</sub> by certain photosynthetic microalgae or blue-green algae, as well as non-phototrophic bacteria [111].

Species	Product	Characteristics	Ref.
Chlorella pyrenoidosa		Tichle mission dation and betweeters containing	[128]
Chlorella pyrenoidosa		composition of the sustainable biocarbon will make it an attractive	[129]
Scenedesmus sp.	Biocarbon	material for a lot of applications, including supercapacitors, CO2	[130]
<i>Graesiella</i> sp. WBG-1		capture, and catalysts for oxygen reduction reaction.	[131]
Chlorella sp., Scenedesmus sp., Spirulina sp., Synechocystis sp.			[132]
Tetradesmus obliquus, Chlorella protothecoides, Chlorella vulgaris	Biostimulants	Sustainable and economical substitute to synthetic liquid fertilizer for promotion of eco-agriculture.	[133]
Chlamydomonas reinhardtii, Chlorella sorokiniana			[134]
Scenedesmus sp. UTEX 1589		They have great biodegradability, biocompatibility, and properties comparable to regular thermoplastics. Being derived from sustainable natural materials, these biopolymers establish to solve the environmental issues caused by petrochemical plastics.	[135]
Nannochloropsis	Bioplastics	Thanks to the combination of their unique characteristics, PHAs	[136]
Spirulina		biodegradability and biocompatibility allow their use in medical	[137]
Chlamydomonas reinhardtii 11-32A		utilization, e.g., in the manufacture of implants, wound dressings, or drug delivery carriers.	[138]

**Table 5.** Comparison of long-term products made with microalgal biomass that can help achieve negative CO<sub>2</sub> emissions.

Species	Product	Characteristics	Ref.
Chlorella kessleri	_	Biocement is a competitive material compared to conventional	[139]
Chlorella vulgaris	Cement	ement products. Its manufacturing is economically and environmentally instified as high temperatures are not required. Biocement is used	
Synechococcus elongatus and Spirulina platensis		to repair damaged structures and to strengthen eroding rock	[141]

## Table 5. Cont.

## 9. Blue Carbon and Phycoremediation

Phycoremediation is the process of harnessing macroalgae, microalgae, and blue-green algae for the removal or bioconversion of toxic and resistant pollutants present in aquatic ecosystems and capturing atmospheric  $CO_2$  as a way of improving the environment [142]. This method, based on natural ecosystems, has been shown to be commercially and environmentally viable thanks to its efficiency and the global abundance of sea/ocean waters. The term 'blue carbon' refers to the  $CO_2$  removed from the atmosphere by oceanic ecosystems, in particular phytoplankton, algae, macroalgae, mangroves, seagrass meadows, and saltmarshes, through the growth of plants and accumulation/embedding of organic matter in soil and sediments. The contribution of natural ecosystems and phytoplankton to atmospheric  $CO_2$  sequestration is presented in Table 6. Microalgae are the largest contributors to this type of  $CO_2$  biosequestration, removing an estimated 12,000 MgCO<sub>2</sub>/km<sup>2</sup>·year [143].

Table 6. Mechanism and contribution of microalgae to the blue carbon concept.

<b>Blue Carbon Warriors</b>	$CO_2$ Sequestration Intensity [MgCO <sub>2</sub> /km <sup>2</sup> ·year]	Total Carbon Sequestration [TgC/year]
Mangroves	829	31.45
Salt marshes	799	11.12
Seagrasses	506	44.02
Cultured macroalgae	1500	0.68
Coral reefs	543	16.5
Wild macroalgae	150	173
Microalgae	11,280	Not available

In the oceans, carbon can be sequestered in the natural environment or through controlled cultures of microalgae/macroalgae. Developing blue carbon strategies, initiatives, and projects can bring many benefits, e.g., carbon capture and storage, improvement of the trophic state of oceans (removal of the excess nutrients that cause eutrophication), and improvement of sea ecosystem health (restoration of marine life) [144]. Controlled cultures of microalgae not only benefit the environment, but can also provide marketable products, such as alternative foodstuffs, diet supplements, low-emission animal feed, and other algae-derived products (including those that fix CO<sub>2</sub> in the long term) [145]. Notably, seas and oceans are the largest ecosystems that act as a "biological carbon pump", sequestering CO<sub>2</sub> in organic compounds or minerals (mainly through the primary production of phytoplankton). Through this process, each year approx. 10 gigatons of carbon are drawn from the atmosphere into the oceans worldwide [146]. Even minor fluctuations in the proliferation of sea microalgae can influence atmospheric CO<sub>2</sub> levels and global warming.

Debowski et al. [147] have explored ways to improve the trophic state of oceans by removing phytoplankton biomass. Their experiments support the applicability of microalgal biomass from natural reservoirs as a potential substrate in biogas production systems. In addition, they have shown that the choice of growing season for biomass harvest and the related taxonomic structure have a direct impact on the anaerobic processes and their final products [147]. In the same vein, Zhong et al. [148] described ways of using algal biomass to produce biofuels, focusing on *Cyanoprokaryota* sourced from the eutrophicated Lake Taihu in China [148]. Extensive blue-green algal blooms, during which the growing phytoplankton biomass binds significant amounts of CO<sub>2</sub>, are an increasingly common phenomenon in many natural water bodies around the world. Capturing and

utilizing microalgal biomass from natural water bodies can help improve the trophic state of those bodies, while also improving air quality. Microalgal biomass growth in eutrophicated/degraded water bodies can be enormous, sometimes reaching hundreds of tons per day. The work of these authors, as well as that of other researchers, speaks to the growing interest in this organic substrate as a potential source of organic matter for producing biogas [149,150].

However, it is important to note that achieving stable CO<sub>2</sub> biosequestration in water bodies located in the temperate zone and cooler climates throughout the entire growing season is a problematic endeavor. The main barriers are those related to changes in the weather, which directly impact the amount of harvestable biomass, the taxonomic structure of the algae, and the properties/parameters of the resultant organic substrate [151]. Extraction is both technologically and commercially impractical during winter seasons due to the reduced growth, low concentrations of algal biomass in natural water bodies, and frequent appearance of ice cover. Capturing and utilizing microalgal biomass from eutrophicated surface waters may also pose operational and technological hurdles (variable quality and yields of biomass, costs of harvesting) [152].

#### **10. Future and Prospects**

The EU has adopted a highly ambitious strategy for bioeconomy development. Within this framework, microalgae and their prospective applications in various fields represent a crucial biological resource. In particular, microalgae are currently being promoted for their wide-ranging applications in environmental technologies, bioenergy production, and as a source of valuable nutrients for humans and animals [153]. The microalgae sector will gain a growing position in the EU's blue bioeconomy and has great growth potential, especially in areas near the coast. The EU's blue algae industry has yearly revenue of EUR 1.5 billion and indirect activities (research, etc.) contribute an additional EUR 240 million [154].

In the EU, algal biomass (mainly macroalgae) is largely harvested from natural water bodies. There has been a noted reduction of populations and species, that are commercially exploited in the EU. This is mainly associated with global warming, overexploitation and harvesting of biomass, environmental degradation of aquatic ecosystems, and displacement of endemic species that leads to non-native species rapidly spreading [151]. Therefore, it is necessary to build and operate dedicated facilities for algal biomass production. Microalgae have a competitive advantage, owing to their capacity for efficient photosynthesis, high rate of biomass growth, resistance to harsh environmental conditions, and ability to metabolize many pollutants [155]. Microalgae aquaculture has been shown to achieve the environmental benefits of phycoremediation, while also meeting the increasing demand for algal biomass and reducing pressure on wild populations [156].

It is thus clear that there is a need for solutions that improve the technological, environmental and commercial viability of technologies for producing and utilizing microalgal biomass. However, more research is needed to assess the full environmental impacts of such systems; water, energy and land use; risk of releasing invasive species into the environment; and perception/awareness among local communities. In the EU, unsuitable climate conditions are an additional barrier to large-scale and effective production of microalgal biomass [157]. This directly induces the obligation of preparing such facilities with solutions that assure the appropriate thermal and light settings—crucial factors in microalgae growth. However, these additions make the cost associated with investment and operating increase significantly [158].

A proven way to improve economic efficiency is the use of waste, including wastewater and exhaust gases, as basic components of culture medium [159]. Therefore, a promising solution is to integrate microalgae biomass production systems with municipal management facilities, wastewater treatment plants or agricultural or utilization biogas plants. These types of installations can ensure the right amount and quality of nutrients, including biogenic compounds, and provide a source of carbon dioxide and allow the use of waste heat [160]. Important aspects supporting and stimulating the development of  $CO_2$  capture systems by microalgae are legislative actions leading to GHG emission reduction and supporting the development of renewable energy sources (RES). An example is the requirements for the share of BIO components in liquid fuels, which require a wider use of biofuel technologies [161]. The EU policy aims to increase the share of RES in the energy mix and to reduce  $CO_2$  emissions, which is a challenge for all member states. This balanced approach is not changed drastically by the current situation related to limited access and rising prices of conventional energy carriers. The Indirect Land Use Change Impacts (ILUC) reports review the approach taken so far and challenge the ecological viability of crop-based bioenergy production. Therefore, it is necessary to search for and implement solutions based on the use of advanced biofuels produced from non-food raw materials. Microalgae are mentioned at the top of the list of potential raw materials for the production of biofuels [162].

Biosequestration of  $CO_2$  by microalgae is a biological process, the course and effectiveness of which are influenced by many environmental, technological, and operational factors. Climatic conditions, the intensity and duration of insolation, temperature, as well as the availability of a natural and unlimited water source are of great importance, especially for the economics of the process [163]. The biotechnological factors include the use of selected strains of microalgae and the implementation of molecular engineering techniques to increase the efficiency of photosynthesis, improve the tolerance of microalgae to difficult and changing environmental conditions, and increase the rate of biomass growth and removal of pollutants [164]. The technological and operational parameters concern the lighting method, the type and method of dosing culture medium, the intensity of gas feeding, the degree of their preliminary purification, the type of photobioreactor, and the method of microalgae biomass separation [165]. The most important issue, however, is the optimization of the technological system for  $CO_2$  biosequestration by microalgae towards achieving the technological and economic efficiency of the process.

#### 11. Conclusions

The use of microalgae biomass for industrial purposes, including  $CO_2$  capture, is not a new idea, but has been systematically developed for many years. Due to their features and characteristics, these microorganisms are seen as a prospective alternative to the chemical and physical  $CO_2$  capture methods. However, the widespread and dynamic development of this type of technology is still very limited. The most important factor hindering the widespread implementation of these solutions is still too low technological readiness level and insufficient large-scale verification tests. The observed dynamics of investments are low and do not correspond to the rank assigned to microalgae technologies. It should be clearly stated that the current efficiency of microalgae technology is too low to compete with other  $CO_2$  capture techniques or the production of conventional energy carriers. An important factor is also the volatility and instability of energy prices and  $CO_2$  emission allowances.

The main barriers to the development of microalgae technology are the very complex and multi-variable nature of microalgae cultivation, as well as the lack of sufficient data from installations operated in commercial conditions, which in many cases prevents a reliable assessment of the life cycle. There is also a lack of sufficient legal and subsidy support for such innovative installations. The increase in efficiency can be seen in the implementation of optimization techniques, the use of genetic engineering and the intensification of production with advanced monitoring and process control techniques. However, considering the long-term environmental, energy, and climate policy of the EU, technologies based on the use of microalgae should still be considered as very prospective. Their development is supported both by inclusion in the applicable strategies of the future, as well as financial support for research projects aimed at optimization and improvement of these types of  $CO_2$  capture techniques.

It must be noted that the scale and dynamics of microalgae technologies development in the future depends on many factors that are difficult to predict. These include aspects related to climate policy, the evolution dynamics of competitive and alternative technologies and, above all, the economic aspects of such solutions.

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### Abbreviations

$CO_2$	carbon dioxide,
GHG	greenhouse gas,
EU	European Union,
EC	European Commission,
EU ETS	European Union's Emissions Trading Scheme,
LULUCF	Land Use, Land Use Change and Forestry,
ESR	Effort Sharing Regulation,
RED	Renewable Energy Directive,
EED	Energy Efficiency Directive,
AFID	Alternative Fuels Infrastructure Directive,
CBAM	Carbon Border Adjustment Mechanism,
RES	renewable energy sources,
ILUC	Indirect Land Use Change Impacts,
CCM	carbon-concentrating mechanism,
PBRs	photobioreactors,
TAP medium	Tris-Acetate-Phosphate medium,
SE medium	soil extract medium,
IMC-CO <sub>2</sub> PBR	Immobilized microalgae-based photobioreactor for CO <sub>2</sub> capture,
PHAs	Polyhydroxyalkanoates

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