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Algae-based bioenergy production aligns with the Paris agreement goals as a carbon mitigation technology

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Abstract

Strategies to mitigate climate change have been developing and applying in the productive sector. Carbon capture and storage technologies might decrease the impact of CO₂ emissions on the environment. Biological technologies are an important tool to mitigate CO₂ emissions and microalgae cultivation emerges as a promising alternative, due to the important role of these organisms on the environment, the capacity of growing in different conditions, and the possibility of converting the microalgae biomass into a wide range of value-added products and biofuels. This study evaluated the potential algae-based CO₂ mitigation by coupling industrial flue gas of a Brazilian cement plant to a microalgae cultivation system. The biodiesel production from microalgae biomass is also investigated to replace fossil fuels. The microalgae plant facility was projected to occupy a reminiscent area of 3.8 ha in the cement plant boundary. Two different mitigation scenarios were analyzed and the results showed that by using 15% of intermittent CO₂ input from the cement industry in the microalgae cultivation system it is possible to mitigate 1268 tCO₂ year⁻¹ and to produce 2317 L year⁻¹ of biodiesel. This study provides support information to decision-making to implement carbon capture strategies in the future carbon market to mitigate the environmental impacts of climate change.

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1. Introduction

The use of non-renewable energy sources over the last decades has been causing environmental concerns. The development of sustainable technologies and products emerges as an alternative to overcome the depletion of natural resources, contributing to a carbon-neutral economy transition.

Parties of the United Nations Framework Convention on Climate Change (UNFCCC) extended a landmark agreement to combat and mitigate climate change at COP 21, realized in Paris in 2015. The Paris Agreement aims to strengthen the global effort to keep the global temperature below 2 °C compared to pre-industrial levels and to limit the temperature increase even further to 1.5 °C. Additionally, the agreement also aims to implement financial mechanisms to increase the ability of countries to deal with the transition to a low carbon economy through decreasing greenhouse gases (GHG) emissions and implementing climate-resilient pathways [1].

The Nationally Determined Contribution (NDC) under the Paris Agreement is a document that embodies each Party country to communicate how it will reduce the national emissions aiming to achieve the long-term goals to mitigate climate changes. Brazil's NDC extended the signed commitments of the former Kyoto protocol and reaffirms the country's commitment to reduce total net greenhouse gases (GHG) by 37% in 2025 and the total Brazilian emissions by 43% in 2030 [2].

The Brazilian industrial sector was responsible for emitting 70.7 Mton of CO_{2eq} in 2020, which corresponds to 17.8% of emissions. Among them, the transport sector was responsible for 45.1% of the total emissions against the total of 32.2% of other sectors' emissions, such as agriculture, energy services, electricity, and fugitive emissions [3]. The remaining 4.9% are emissions from the residential sector. However, Brazil is a developing economy increasing its industrial park and the adoption of sustainable practices should be a priority.

One of the major contributors to the release of anthropogenic CO₂ into the atmosphere is cement manufacturing. The cement industry is highly energy consuming and GHG emitter. Almost 70% of CO₂ emissions in a cement industry occur during clinker production, resulting from the decarbonation of raw material during the calcination process. The remaining emissions result from the combustion of fossil fuels to power the manufacturing, indirect emissions from electricity consumption, and those related to the transport of raw materials [4]. The transport mode in Brazil favors a higher CO₂ emission since 96% of cement is transported in diesel trucks [5]. Currently, the Brazilian cement industrial park is composed of 100 cement plants, totalizing an installed production capacity in the order of 100 million tons per year [6]. Considering that the specific emission in Brazil is 565 kg CO₂ ton⁻¹ of produced cement [5], the potential annual emission is around 57 million tons of CO₂ in one year. Therefore, it is essential to focus on the development of new strategies to reduce carbon emissions and to increase the production of bioenergy to replace fossil fuels.

Some strategies for carbon capture and storage have been developed over the years to mitigate environmental damage caused by CO₂ emissions. Among biological technologies, microalgae cultivation emerged as an attractive alternative to carbon capture [7].

Microalgae are eukaryotic or prokaryotic organisms, with high biomass productivity, compared with traditional crops. They can grow in different kinds of resources, from freshwater, seawater, and wastewater, using non-arable lands for their cultivation, promoting the remediation and valorization of different types of streams [8]. In addition, microalgae can be grown throughout the year, and their biomass production provides the mitigation of GHG, due to the high photosynthetic rates and the potential of coupling the cultivation system with industrial flue gas emissions [9]. Furthermore, microalgae have arisen as a very promising alternative for producing a wide range of high-value compounds and bioenergy, and some studies have shown the potential of these organisms for biodiesel production [10].

In this context, this work aims to analyze the algae-based carbon capture strategy from the cement industry, by coupling the microalgae cultivation system to the flue gas emissions and ultimately using the microalgae biomass as feedstock for biodiesel production.

2. Methods

2.1. Biomass production

A strain of freshwater microalgae represented by a *Chlorella vulgaris* was selected to be cultivated for biomass production due to its high growth rate, production of large amounts of lipids and valuable compounds [11] and to its ability to tolerate high concentrations of NO_x and SO_x, that composes the cement flue gases [12,13].

To simulate the microalgae growth, it was applied a derived Monod growth model [14], using different CO₂ concentrations in a tubular photobioreactor designed for this study. The model was simulated using the MATLAB/Simulink software®. According to He et al. [14], the kinetic model used has the following assumptions: (1) biomass was produced in a homogeneous system; (2) CO₂ concentration and light intensity were the limiting factors that influenced the growth of microalgae; (3) the relationship between the partial pressure of CO₂ and its equilibrium concentration in the liquid phase was modeled by Henry's Law. The Eqs. (1)–(3) summarize the kinetic assumptions of the model.

$$\frac{dX}{dt} = \frac{S}{S + K_s + S^2/K_I} \times \frac{I}{I + K} \times \mu_{max} \times X \quad (1)$$

$$I = \frac{I_0}{A \cdot X} (1 - e^{-A \cdot X}) \quad (2)$$

$$\frac{dX}{dt} = K_{LA} (P/H - S) - Y_{S/X} \times \frac{S}{S + K_s + S^2/K_I} \times \frac{I}{I + K} \times \mu_{max} \times X \quad (3)$$

where, X is the microalgal biomass concentration (kg m⁻³); S is the dissolved CO₂ concentration (mol m⁻³); I is the average light intensity (mmol m⁻² s⁻¹); I_0 is the surface light intensity (mmol m⁻² s⁻¹); A is the coefficient (m³ kg⁻¹); P is the CO₂ partial pressure in the gas phase (Pa); μ_{max} is the maximum specific growth rate of microalgae (h⁻¹); K_s is the Michaelis–Menten constant of CO₂ (mol m⁻³); K_I is the inhibition constant of flue gas (mol m⁻³); H is Henry's constant of CO₂ (Pa m⁻³ mol⁻¹); K_{La} is the mass transfer rate (h⁻¹); K is the Michaelis–Menten constant of light intensity; and $Y_{S/X}$ is the yield coefficient (mol CO₂ kg biomass⁻¹).

The kinetic parameters used for the simulation of microalgae growth are summarized in Table 1.

Table 1. Kinetic parameters used in microalgae growth simulation.

Parameter	Description	Value	Units
μ_{max}	Specific maximum growth rate	0.07	h ⁻¹
K_d	Mortality rate	0.028	h ⁻¹
K_s	Michaelis–Menten constant for or CO ₂	0.00021	mol m ⁻³
K_I	CO ₂ inhibition constant	10	mol m ⁻³
K	Michaelis–Menten for luminous intensity	14	μmol m ⁻² s ⁻¹
K_{LA}	Mass CO ₂ throughput	17	h ⁻¹
H	CO ₂ Henry Constant	3,202	Pa m ³ mol ⁻¹
$Y_{S/X}$	Growth coefficient	100	(mol CO ₂) (kg biomass) ⁻¹
A	Constant	14.7	m ³ kg ⁻¹
I_0	Light intensity	41,085	μmol photons m ⁻² s ⁻¹
CO ₂ (A)	Atmospheric CO ₂ concentration	0.0004	Volumetric fraction
CO ₂ (G)	CO ₂ concentration in effluent gases	0.15	Volumetric fraction
$X(0)$	Initial biomass concentration	0.1	kg m ⁻³
$S(0)$	Initial concentration of dissolved CO ₂	0.013	mol m ⁻³

To overcome the microalgae growth inhibition caused by medium acidification due to continuous exposure to flue gas, the model considers an on-off flue gas input mode, in which flue gas was modeled to pulse into the photobioreactors at a specific frequency of 1 min gas-on (15% CO₂), and 29 min gas-off (0.04% atmospheric CO₂) [14].

2.2. Carbon capture case study

In this work, it was designed a carbon capture system based on microalgae cultivation coupling to flue gases from a cement industrial plant located in the city of Cubatão, São Paulo, Brazil. Dataset was obtained from the public “Project Design Document” sent to the UNFCCC and the Brazilian Interministerial Commission on Global Climate Change (National Authority Designated Brazilian Government) for the approval of projects under the Clean Development Mechanism (CDM) of the former Kyoto Protocol to obtain carbon credits. This document and data were chosen as a base to obtain insights about future prospection and implementation of carbon mitigation mechanisms to achieve the Paris Agreement goals. The CDM project sent to UNFCCC aimed to replace fossil

fuel with natural gas in the blast-oven slag dryer used in the manufacture of cement, thus reducing carbon dioxide emissions. The project started in 2004, with an expected operating lifetime of about 30 years.

In this study, two different scenarios described in the CDM project sent to the UNFCCC were used to calculate the amount of CO₂ mitigated by microalgae cultivation in the cement industry:

1. The base scenario, that corresponds to the emission of about 22,461 tCO₂ per year, using fossil fuel;
2. The CDM scenario, that corresponds to the emission of about 12,000 tCO₂ per year, using natural gas.

2.3. Microalgae downstream process

The downstream process considered biomass harvesting, drying, cell disruption, lipid extraction, oil refining, and transesterification process. The production of biodiesel was estimated according to the adapted methodology published by Branco-Vieira et al. [15]. Briefly, the dried biomass was milled in a ball mill machine to release all cellular components and total oil content was recovered by using a supercritical CO₂ method, assuming that only triglycerides are obtained from the biomass, with an efficiency of 95% of extraction. In terms of microalgae oil content, it was considered an amount of 22% of total lipids in *C. vulgaris* cells [16]. The lipids were converted into fatty acid methyl esters (FAME) or biodiesel, via an alkali-catalyzed transesterification reaction.

3. Results and discussion

3.1. Biomass production

The microalgae growth was simulated according to the model during 12 days of cultivation, using two different CO₂ concentrations. The microalgae biomass production using atmospheric CO₂ concentration (0.04% of CO₂) showed a yield of 0.408 kg m⁻³ of biomass on the 12th day of cultivation, and an average productivity of 0.254 kg m⁻³ d⁻¹ (Fig. 1). On the other hand, the production of microalgae biomass fed with 15% of CO₂ from cement plant flue gases was around 1.44 kg m⁻³, which corresponds to the average productivity of 0.681 kg m⁻³ d⁻¹ (Fig. 1). The values achieved using flue gas correspond to an increase of 28.33% on the microalgae growth rate and 37.30% on microalgae daily productivity.

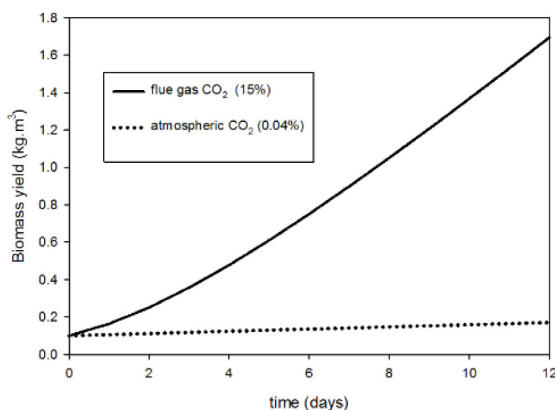


Fig. 1. Microalgae biomass yield during 12 days of cultivation.

An experimental study conducted by Kumar et al. [9] to verify the growth of *Chlorella* sp. using different kind of wastewater and 6% of industrial CO₂ emissions has shown average biomass productivity of 0.6 g/L, similar to that found in this study. Although the simulated parameters have not considered the presence of other potentially toxic gases to microalgal growth, some studies in the literature have verified that a couple of microalgae strains support certain concentrations of these gases and sustain considerable growth. In the same study conducted by Kumar et al. [9], a concentration of 180 ppm of SO_x and 250 ppm of NO_x was considered, and the microalgae cultivation has achieved a reasonably high biomass yield.

On the other hand, Kumar et al. [17], have studied the growth of *Chlorella sorokiniana* for CO₂ sequestration from industrial flue gas containing 15.6% of CO₂ and 120 mg L⁻¹ of H₂S and concluded that the high concentration of CO₂ and H₂S had an inhibitory effect on the growth of *C. sorokiniana*, and suggested a previous treatment on the flue gas before injecting it to the microalgae culture medium to maximize the algal biomass production.

3.2. Carbon capture case study: Cement plant flue gas mitigation

The cement industry used as a case study has a total area of 9.8 ha with an available zone of 3.8 ha for the installation of microalgae upstream and downstream facilities. An area of 3.3 ha was destined for the operation of the PBRs, and the remaining 0.5 ha for the downstream process of biomass. The PBR designed for microalgae cultivation was set to have a tubular shape. The configuration of PBR consists of 20 tubes distanced at 0.115 m vertically, 5 rows of a set of vertical line tubes distanced at 0.25 m. The dimensions of each PBR module are 60.36 m long, 2.23 m in width, and 3.49 m in height (Fig. 2A). The total volume of each PBR module is 34 m³. To support this volume, an area of 134.3 m² of soil is occupied. With an available area of 3.3 ha, it would be possible to build 150 PBR modules totalizing 5101 m³ of culture (Fig. 2B).

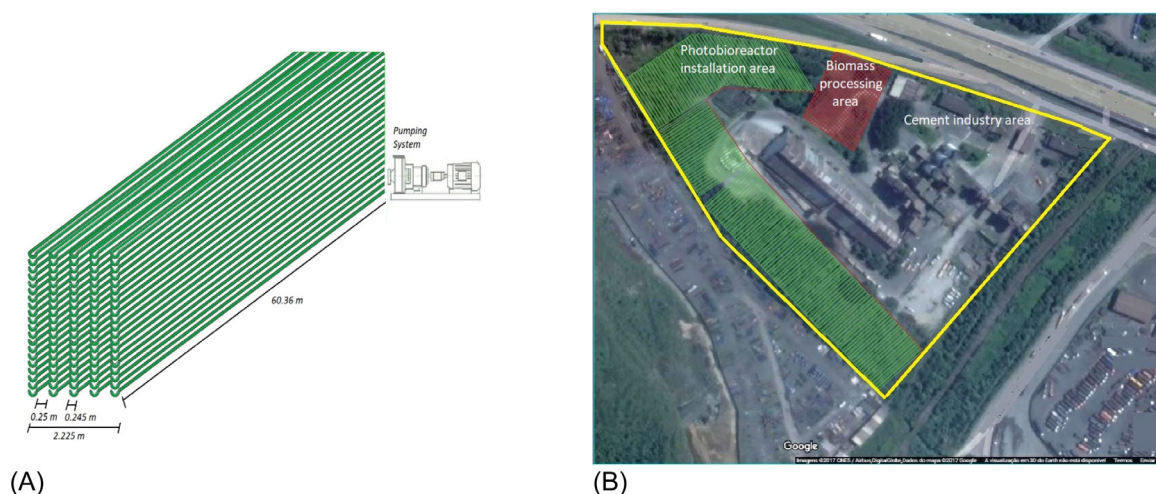


Fig. 2. Industrial microalgae cultivation process and biodiesel production plant. (A) Tubular photobioreactor module conception. (B) Upper view of the cement plant indicating the total area to be used for microalgae cultivation and processing.

Source: Adapted from Google earth [18].

The total amount of biomass that it will be possible to achieve when microalgae are cultivated under atmospheric CO₂ is 473 tons of biomass per year. Otherwise, when 15% of CO₂ from industrial flue gas is used to feed the microalgae cultivation system, it would be possible to achieve a maximum of 1268 tons of biomass per year. Considering the proposed model, it is necessary about 1 kg of CO₂ for the production of 1 kg of dry biomass of *C. vulgaris* [19] which corresponds to mitigation of about 0.68 kg m⁻³ of CO₂ per day of microalgae growth. Therefore, these values also correspond to an amount of 1268 tCO₂ year⁻¹ of mitigated CO₂ using 15% of CO₂ from the flue gas to microalgae cultivation.

Considering the base scenario of this study, which is used fossil fuel as the primary energy source in the cement production system, the total CO₂ mitigation corresponds to 5.65% of the annual emissions, when 15% of industrial flue CO₂ is applied to the culture medium. Otherwise, in the CDM scenario, in which the use of fossil fuel was replaced by natural gas on the CDM project, the additional algae-based CO₂ mitigation reaches the value of 10.57%.

Overall, the algae-based carbon capture efficiency depends on the microalgae strain, type of cultivation system, the CO₂ concentration, design, and operating conditions of PBR. The study conducted by Clément-Larosi re et al. [20] has shown that *C. vulgaris* is a strong candidate for industrial CO₂ remediation, obtained a maximum CO₂ removal rate of 0.98 gCO₂ L⁻¹ d⁻¹ and the highest biomass concentration of 4.14 g DW L⁻¹ at 13% CO₂. Seyed Hosseini et al. [21] have studied the possibility of using *C. vulgaris* for CO₂ sequestration in Alberta, Canada, using wastewater as a culture medium and in the presence of 20% of CO₂ in the total volume of the PBR. The

authors have achieved mitigation of 100% of CO₂ during 36 h of cultivation. Klinthong et al. [22] have achieved a maximum CO₂ removal efficiency of 55.3% at 0.15% of CO₂ in the culture medium of *C. vulgaris*.

Furthermore, Quelhas et al. [23] have analyzed the productivity of *Phaeodactylum tricornutum* in different PBR volume to CO₂ biofixation and the results showed that the CO₂ mitigation efficiencies ranged 41 to 60% in cultures where the CO₂ was introduced into the PBR, corresponding to 2.3 to 2.5 g of fixed CO₂ per g of biomass.

A recent study published by Llamas et al. [24] reported that the utilization of microalgae carbon capture technology could be a promising tool to apply in the future carbon pricing mechanism foreseen in the Paris agreement.

3.3. Biodiesel production

In this study it was analyzed the potential of producing biodiesel from microalgae biomass after harvesting and drying the biomass cultivated at 15% of CO₂. The production of biodiesel was performed using the modified method described in [15]. The total content of lipid for *C. vulgaris* considered in this study was 22% and the maximum volume of lipid that can be recovered by the microalgae biomass using the SC-CO₂ is 2090 kg year⁻¹. After lipid extraction, the oil is refined and biodiesel production is performed by using the alkali-catalyzed transesterification reaction. The maximum potential amount of biodiesel achieved is 2037 kg year⁻¹ or 2317 L year⁻¹ using an oil density of 880 kg m⁻³.

Several studies have analyzed the production of microalgal lipids to biodiesel production. Branco-Vieira et al. [10] have analyzed the production of *Phaeodactylum tricornutum* for biodiesel production using atmospheric CO₂ during 14 days of cultivation and achieved average productivity of 0.13 kg m⁻³ d⁻¹. Branco-Vieira et al. [15] modeled the annual production of 181 tons of algal biomass per year, using the same productivity of 0.13 kg m⁻³ d⁻¹, and estimated an amount of 15 tons of biodiesel per year.

Xia et al. [25] have analyzed the lipid productivity of *Chlorella sorokiniana* cultivated in a range of 5%–15% of CO₂ and found maximal productivities at 10% CO₂. Yusof et al. [26] have investigated the possibility of modifying lipid contents in *C. vulgaris* by varying the amount of carbon dioxide and light. The authors found that some fatty acids increased when the amount of CO₂ was raised from 1 to 10%.

Indeed, the microalgae ability of industrial carbon capture, considerably improves the environmental performance and the carbon footprint of the process. Additionally, the valorization of the microalgae compounds into the appropriate form of biofuel and other algal added-value products contributes to increase the economic valorization of the process. The possibility of using microalgae cultivation for carbon biofixation contributes to the sustainable development of any industrial bioprocess, making this approach a great and competitive promise to the carbon market foreseen in the Paris agreement.

4. Conclusions

The algae-based carbon capture alternative was analyzed in this study, using two different scenarios of CO₂ mitigation from a cement plant located in Cubatão, São Paulo, Brazil, and the microalgae biomass production was used for biodiesel production. Simulations indicated that *C. vulgaris* exhibited promising growth using 15% of CO₂ from cement industry flue gas, can generate a maximum microalgae biomass of about 1268 tCO₂ year⁻¹, reaching the same amount of CO₂ mitigation. These results indicated that the total CO₂ mitigation corresponds to 5.65% and 10.57% of the annual emissions in the base and CDM scenarios, respectively. The total amount of biodiesel produced was about 2317 L year⁻¹. In this regard, the utilization of microalgae-based CO₂ biofixation was identified as a good alternative to traditional carbon capture technologies, since microalgae biomass is highly versatile and can be used to generate valuable compounds and biofuels, and could be a competitive alternative in the future emission rights market.

CRedit authorship contribution statement

M. Branco-Vieira: Investigation, Formal analysis, Validation, Writing – original draft. **M.P.C. Lopes:** Investigation, Formal analysis, Validation, Writing – review & editing. **N. Caetano:** Supervision, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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