Nanobiotechnology: advances in the use of nanomaterials to increase CO₂ biofixation by microalgae

Michele Greque Morais (✉ migreque@yahoo.com.br)

Federal University of Rio Grande: Universidade Federal do Rio Grande

Bruna Pereira Vargas

Federal University of Rio Grande: Universidade Federal do Rio Grande

Bruna Silva Vaz

Federal University of Rio Grande: Universidade Federal do Rio Grande

Bruna Barcelos Cardias

Federal University of Rio Grande: Universidade Federal do Rio Grande

Jorge Alberto Vieira Costa

Federal University of Rio Grande: Universidade Federal do Rio Grande

Research Article

Keywords: adsorbents, bioprocess, carbon dioxide, mitigation, nanotechnology

Posted Date: February 24th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-206067/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Microalgae through photosynthesis can convert atmospheric CO₂ into biomass to produce biofuels and high value-added bioproducts. the improvement of the cultivation systems helps in the conversion of gases into biomass and, consequently, increase microalgal productivity. Recently, studies involving the technology of physical adsorption with nanomaterials have shown promising results in increasing the CO₂ biofixation by microalgae. Polymeric nanoparticles produced by the electrospraying technique stand out as potential adsorbent materials for CO₂ capture due to the high surface area per unit volume formed by many active sites that increase the gas adsorption capacity in a liquid medium. The interactions between plant cells and nanomaterials have been revealed the potential of nanobiotechnology to reduce environmental pollution and contribute to sustainability. Moreover, the development of these methodologies can contribute to the viability of large-scale microalgae cultivations for CO₂ mitigation. Based on this, the objective of this review is to address the advances of nanobiotechnology to increase CO₂ biofixation by microalgae. The potential of adsorbent nanoparticles developed by the electrospraying technique and the key points for applying it for this purpose are also discussed.

Highlights

The use of physical and biological methods reduces atmospheric CO₂.

Polymeric nanoparticles can adsorb CO₂ in microalgae cultivation.

Electrospraying is an efficient technique for nanoparticles development.

Electrosprayed nanoparticles production depends on the association of many factors.

1. Introduction

The accumulation of greenhouse gases (GHG) in the atmosphere, such as methane (CH₄), nitrogen oxide (NO_x), and carbon dioxide (CO₂) from anthropogenic activity, is associated with risks to the ecosystem and human health. Among GHGs, CO₂ receives more attention because it represents 77% of this volume, due to the economy based on the burning of fossil fuels, in which this gas corresponds to the main compound formed (Nocito and Dibenedetto 2020). Global CO₂ emissions related to energy production reached 33.2 billion tons in 2019. This fact reflects the harmful effects of industrialization and urbanization. Based on this, it is recommended to replace current industrial processes with “low-carbon” technologies to reduce GHG emissions by up to 80% by 2050 (IEA 2019; Ikedi 2018).

An alternative to reduce or stabilize CO₂ emissions is to capture post-combustion carbon. Post-combustion processes can be installed in energy production plants with minimal change in the design or operation of the plant and allow maintenance flexibility without interrupting the plant's operation (Mansour et al. 2016). The main strategies for removing post-combustion atmospheric carbon are based

on physical, chemical, or biological systems. Industrially, chemical processes are the most used, due to the low cost and ease of application on a large scale (Lam et al. 2012). Physical processes mainly use membranes, activated carbon and zeolites (Leung et al. 2014). Biological treatment can be carried out on the industrial scale by microalgae, but still faces challenges associated with the high cost of installation and maintenance (Acién et al. 2012).

The association of CO₂ mitigation methods has been studied to achieve greater energy efficiency together with cost reduction. Microalgae technology has contributed to “recycle” CO₂ combined with the concept of biorefinery (Aresta et al. 2013). Interesting results were obtained by associating chemical absorption and biological process with different microalgal strains (Cardias et al. 2018; Rosa et al. 2018). In addition, CO₂ biofixation associated with physical adsorption using membranes (Rahaman et al. 2011) and, recently, with nanofiber technology, has shown even more promising results (Comitre et al. 2021; Vaz et al. 2019, 2020).

Nanobiotechnology stands out as the beginning of a new era for the development of science around the world (Agarwal et al. 2019). In this sense, Vaz et al. (2019) developed polyacrylonitrile (PAN) nanofibers for CO₂ adsorption. The authors observed that the addition of iron oxide nanoparticles (NPsFe₂O₃) in the nanofibers intensified the gas adsorption capacity by the nanostructures, mainly by increasing the material's porosity. This technology can be associated with microalgal cultivation with a 57% increase in the rate of CO₂ biofixation, compared to assay without nanofibers. Polymeric nanoparticles also stand out as potential CO₂ adsorbents (Beltzung et al. 2018), and studies on the performance of these nanomaterials associated with the biological process are innovative. Moreover, compared to the usual metallic nanoparticles, polymeric nanoparticles do not appear to have cytotoxic effects on microalgae, when exposed in the long term (Jeevanandam et al. 2018).

The electrospraying technique is a bottom-up method where the polymeric solution is sprayed to produce nanoparticles (Khan et al. 2019). The combination and control of the parameters used in the technique, such as solution viscosity, electrical potential, injection capillary diameter, among others, guarantee the formation of stable nanoparticles and with several active sites for CO₂ adsorption (Niu et al. 2020).

Significant advances have been observed on an academic and industrial scale in terms of reducing CO₂ emissions into the atmosphere. However, the mitigation potential of existing technologies is not equivalent to emissions. Therefore, the integrated use of biological, physical, and chemical systems plays an important role not only for the capture but also for the use of carbon and conversion to other forms of energy, such as biofuels (Nocito and Dibenedetto 2020). Based on this, the objective of this review is to address the advances of nanobiotechnology to increase CO₂ biofixation by microalgae. The potential of adsorbent nanoparticles developed by the electrospraying technique and the key points for applying it for this purpose are also discussed.

2. Technologies Of Co Mitigation

CO₂, like water, is the result of combustion processes, biological or chemical, and is the form of carbon most used in nature by microorganisms and plants to form thousands of compounds that make up its structure. However, the natural carbon cycle is not able to regulate the high anthropogenic CO₂ emissions that occur annually (Aresta et al. 2013). It is estimated that CO₂, which originated from energy production processes, contributes to over 60% of global warming. As a result, currently, around 5–7 million tons of CO₂ per year are captured and stored underground, and there is no knowledge of the consequences of this practice for human health and the environment (Ali et al. 2019; Nocito and Dibenedetto 2020). The treatment of this greenhouse gas can occur by chemical, physical or biological means (Fig. 1). Some are industrially consolidated, and others are growing.

2.1 Chemical methods

Traditional industrial CO₂ capture and separation processes use systems based on chemical absorbents such as amines, carbonates, aqueous ammonia, and ionic liquids. The chemical reaction is selective for the basic groups present in the absorbent molecules. The advantage of the absorption process is its low cost, easy handling, and large-scale application (Koronaki et al. 2015).

However, the impacts of amines, which are the most widely used absorbents, arise since their production. Chemical synthesis through the reaction between ethylene oxide and ammonia involves energy consumption and generates direct or indirect CO₂ emissions, which is precisely the problem to be treated (Luis 2016). Besides, the recovery of the absorbent takes place in a desorption column under a low pressure and temperatures of 100–140°C, requiring even more energy (Koronaki et al. 2015). Another challenge is the corrosion of equipment, which generates loss of solvents, in addition to the formation of volatile degradation compounds (Leung et al. 2014).

Studies have associated chemical fixation with physical and/or biological methods taking advantage of the positive aspects of chemical absorbents. The functionalization of polymeric nanofibers with amines, for example, increases the adsorption capacity of these materials. Polystyrene and polyurethane nanofibers produced by electrospinning show an increase of up to 96% in the CO₂ adsorption capacity when functionalized with polyethyleneimine (Zainab et al. 2018). As for biological processes, the addition of low concentrations (0.02 to 0.5 mL L⁻¹) of chemical absorbents as monoethanolamine and diethanolamine show an increase in the rate of CO₂ biofixation by microalgae and changes in the biomass composition, as the content of carbohydrates, for example (Rosa et al. 2018; Cardias et al. 2018).

2.2 Physical methods

In physical methods, CO₂ binds to the surface of a solid adsorbent, a mechanism known as adsorption. The best-known adsorbents are activated carbon, polymeric membranes, zeolites, and calcium oxides. High surface area, selectivity, and regeneration capacity are essential criteria for choosing the adsorbent (Leung et al. 2014). Membranes have been widely used for their ease of application and good

performance, in addition to being compact due to the need for small installation space. They are typically produced in layers of 0.1 to 2.0 μm using polymers, due to the high selectivity of these materials to the treated gas (Ng et al. 2013; Nocito and Dibenedetto 2020).

The membranes can be adapted in energy production plants at the end of a flue gas flow in a simple way, operating by gas solution/diffusion mechanisms through the motive force provided by the partial pressure (Li et al. 2017). The disadvantage of using membranes for gas separation is the loss of performance due to exposure to high flue gas temperatures. Besides that, the need for a pressure gradient that is equivalent to energy expenditure, so that some components permeate through the membrane while others are retained (Abdolahi-Mansoorkhani and Seddighi 2019; Li et al. 2017).

Zhang et al. (2017) developed membranes composed of PAN nanofibers by the electrospinning technique for CO_2 adsorption. The study showed good thermal stability and tensile strength, maintaining 92% the ability to retain CO_2 after 20 cycles of use at high desorption temperature (105°C for 40 min each cycle). Vaz et al. (2019) developed PAN nanofibers with the electrospinning technique and observed an increase in the CO_2 adsorption efficiency with the addition of NPsFe_2O_3 to their structure. According to Abdolahi-Mansoorkhani and Seddighi (2019), nanoparticles are added to the membranes to increase the porosity and contact area and, consequently, obtain greater efficiency for gas removal. The authors noted that adding up to 20% (w w^{-1}) of calcium carbonate nanoparticles to the membranes can increase the removal of CO_2 up to 9% and hydrogen sulfide from the mixture up to 8% of that makes up natural gas, compared to membranes without the nanoparticles.

This new generation of nano-absorbent materials has a high potential for application in adsorption processes due to its ability to work in extreme temperatures and several reuse cycles without losing efficiency. These nanomaterials can be developed in an ecological and controlled manner with virtually no waste generated, avoiding environmental contamination (Vaz et al. 2019). Materials produced by electrospinning with aqueous solvents can reduce the use of organic solvents as much as possible. In addition, the production of nanomaterials can be optimized and increased on an industrial scale, based on the principle of multiplying the jets by building equipment with multiple capillaries powered by a single source of polymeric solution (Petrík 2011).

2.3 Biological methods

Phototrophic microalgae are 10–50 times more efficient than terrestrial plants in converting solar energy into chemical energy, which results in growth up to 100 times faster. Several species of microalgae can tolerate high concentrations of CO_2 , and cultivation parameters are studied to optimize the biofixation (Lam et al. 2012).

Among the modifications in microalgal culture to increase the efficiency of CO_2 biofixation are the association with chemical absorption and physical adsorption methods. The addition of chemical absorbents, such as monoethanolamine and diethanolamine, to the microalgae cultivation of *Spirulina* and *Chlorella* showed an increase of more than 60% in the rate of CO_2 biofixation (Cardias et al. 2018;

Rosa et al. 2018). However, all studies indicate that risks of toxicity to microalgal cells depend on concentrations of amines, which limits the use of chemical absorbents.

When physical adsorption is combined with the biological method, the risk of toxicity to cells due to the presence of these compounds that do not belong to the medium is reduced or null, since the main polymers used in the development of nanomaterials for adsorption of CO₂ are not toxic to microalgae (Nguyen et al. 2019). Vaz et al. (2019) observed that up to 0.5 g L⁻¹ of PAN nanofibers containing 4% (w w⁻¹) NPsFe₂O₃ did not inhibit the growth of the microalgae *Chlorella fusca* LEB 111 and increased the rate of CO₂ biofixation by 57% compared to cultivation without nanofibers.

3. Nanoparticles

Nanoparticles comprise solid particles that can be in suspension or as dry materials which have at least one of their dimensions in scale between 10 and 1000 nm. These nanomaterials are developed mainly in the form of spheres, cylinders, disks and tubes (Nagarajan 2008). In addition to shape classification, nanoparticles can also be subdivided into nanospheres and nanocapsules. Nanospheres are solid and massive nanoparticles, while nanocapsules act as a protective wall to cover nanoencapsulated compounds (Khan et al. 2019).

Nanoparticles are subdivided into 4 main categories related to their composition: carbon-based, inorganic compounds, organic compounds, or composite materials. Carbon-based nanoparticles, such as nanotubes and fullerenes, have carbon as their main constituent, while organic nanoparticles comprise all organic matter including polymers, micelles and liposomes, except for carbon materials (Jeevanandam et al. 2018; Khan et al. 2019). Inorganic nanoparticles are developed mainly with metals, metal oxides or semi-conductors. Nanocomposites are formed with the combination of materials such as polymers and metals (Jeevanandam et al. 2018).

The nanoparticles have different characteristics when compared to the same material on the macro scale (Khan et al. 2019). In a nanometric scale, gravitational and frictional forces are reduced, and others begin to act, such as electrostatics, van der Waals, Brownian motion, and quantum mechanics (Nagarajan 2008). The main properties of nanomaterials include high surface area per unit volume; high reactivity; mechanical strength; and a high proportion of atoms on the surface and in nearby layers (Khan et al. 2019; Nagarajan 2008).

Nanoparticles are used in various scientific fields due to their different characteristics. In the environmental area, studies aimed to remove water and air contaminants by application of nanoparticles (Khan et al. 2019). Furthermore, PAN polymeric nanofibers, containing NPsFe₂O₃, can be used to adsorption of greenhouse gases such as CO₂ (Beltzung et al. 2018; Vaz et al. 2019).

The application of spherical nanoparticles in CO₂ adsorption processes has been gaining visibility over the years, mainly due to its high surface area per unit volume, which increases the amount of adsorbing

active sites. In addition, the interactions between contaminants, such as CO₂ and nanoparticles are dependent on other characteristics of nanomaterials as composition, size, morphology, porosity, and polydispersity (Khan et al. 2019). These characteristics are dependent on the polymer chosen, as well as the technique applied for the development of nanomaterials (Beltzung et al. 2018; Khan et al. 2019).

4. Efficient Method For The Development Of Nanoparticles

Nanoparticles are developed by two types of synthesis: top-down and bottom-up. Top-down synthesis comprises an approach in which large molecules are converted into small units that reach the nanoscale. The top-down synthetic route uses mainly physical methods, such as milling, laser fragmentation, deposition by physical vapor, and coacervation. The bottom-up approach is characterized by the development of nanoparticles through the self-assembly of atoms and molecules. Techniques such as reduction by biological agents, sol gel, polymerization, and electrospraying are examples of bottom-up synthesis (Khan et al. 2019).

Over the years, several methodologies for obtaining polymeric nanoparticles have been developed and improved. Techniques such as coacervation, polymerization and electrospraying are employed for the development of nanoparticles composed of polymeric materials. The electrospraying stands out among these techniques due to the several benefits that the method offers. Among the advantages, it can include development of small scale particles in the range of micrometers and nanometers; size distribution of nanomaterials very similar to a monodispersive system; size and shape controlled by setting the parameters of the process; no subsequent drying step is required; use of room temperature; and nanomaterials deposited in a dispersed way, which avoids the agglomeration of particles (Bock et al. 2012; Niu et al. 2020). Moreover, the advantage that most catch the attention of those adept at the technique includes the possibility of scaling up (Niu et al. 2020).

Electrospraying can be applied for the development of nanospheres and nanocapsules (Ibili and Dasdemir 2019; Niu et al. 2020). The basic configuration of the equipment comprises a high-potential electrical power supply, capillary connected to a positive displacement pump, and grounded collector (Niu et al. 2020). Figure 2 shows schematically the equipment used for the electrospraying technique.

The electrospraying principle consists in the application of a high electrical potential between the capillary and the grounded collector. The electric field generated produces electrostatic forces, known as Coulomb forces, which compete with the surface tension of the polymeric solution. When the electrostatic forces reach a critical value, they overcome the surface tension of the polymeric solution drop in the capillary tip, producing a conical-shaped jet, known as Taylor cone. This cone propagates and breaks down into droplets (nanoparticles) that are attracted to the grounded collector, depending on the difference of the electrical charges. The solvent completely evaporates in the path between the capillary and the collector. The production of nanoparticles by electrospraying technique is directly affected by the properties of the polymeric solution, process parameters and environmental conditions. These parameters require rigid control for the reproducibility of the technique (Bock et al. 2012).

5. Parameters That Affect The Development Of Nanoparticles By Electrospraying

Polymeric solution properties include the type of solvent, viscosity, molecular weight, polymer concentration, surface tension and electrical conductivity (Bock et al. 2012). The chosen solvent must solubilize all the polymer, in addition to presenting moderate vapor pressure, allowing rapid evaporation during the tip-to-collector distance (Bock et al. 2012; Niu et al. 2020). The molecular weight of the polymer is strongly related to the concentration and viscosity of the solution. Polymers with higher molecular weight result in viscous solutions, with a higher degree of entanglement in the polymer chains. Thus, it is recommended the use of low-concentrated and viscous solutions, to propagate the Taylor cone in small droplets that are attracted to the collector and deposited in the form of nanoparticles (Bock et al. 2012).

Surface tension and electrical conductivity are properties that also affect the development of nanoparticles. The surface tension of the polymeric solution is the main force that opposes to the electrical potential during the electrospraying technique. Therefore, the applied potential needs to be large enough to overcome the surface tension contributing to the propagation of the Taylor cone. Otherwise, it will occur the jet instability and dripping of the solution in the collector (Bock et al. 2012).

Electrical conductivity contributes to the initiation of the electrospraying process and the morphology of nanoparticles. Low conductive solutions ($\approx 1 \mu\text{S cm}^{-1}$) are recommended and should produce enough current for the development of nanoparticles. High conductivity conditions increase the strength of the electric field, resulting in the elongation of nanomaterials, forming heterogeneous nanoparticles and nanofibers (Niu et al. 2020).

The process parameters include the electrical potential, polymeric solution flow rate, capillary diameter, and tip-to-collector distance (Bock et al. 2012). The electrical potential is the main factor that determines the beginning of the electrospraying technique. The gradient of the electrical potential applied should be sufficient to overcome the surface tension of the polymeric solution drop at the tip of the capillary, promoting the development of the Taylor cone (Niu et al. 2020). A study conducted by Park and Lee (2009) points to the existence of a critical electrical potential (PE_c) value that is dependent on the developed solvent polymer system. In general, the PE_c value for the development of nanoparticles varies between 10 and 20 kV (Ibili and Dasdemi 2019). Values below the PE_c result in the dripping of the polymeric solution in the collector, while the use of PE_c or values above it, result in the development of nanoparticles. The use of potentials far above PE_c promotes the development of nanofibers (Park and Lee 2009).

The flow rate of the polymeric solution affects the size and morphology of the nanoparticles (Niu et al. 2020). Low flow rates ($\approx 600 \mu\text{L h}^{-1}$) are recommended for the electrospraying technique, as they result in complete evaporation of the solvent and contribute to the reduction of the nanoparticle diameter. A high flow rate promotes the formation of non-spherical nanomaterials with a high polydispersity (Ibili and Dasdemir 2019; Niu et al. 2020).

Another parameter that can increase the polydispersity of nanoparticles is the diameter of the capillary, which limits the propagation size of the Taylor cone. The larger the diameter of the cone, the greater the instability of the technique, that increases the size of the nanomaterials and the possibility of dripping the solution in the collector (Bock et al. 2012). Ibili and Dasdemir (2019) developed nanoparticles of polylactic acid and evaluated the capillary diameter between 0.45 and 0.66 mm. The authors observed that capillaries of 0.45 mm promoted the development of homogeneous nanomaterials with a smaller diameter.

Regarding the distance between the capillary and the collector, when constant electrical potential is applied, a small distance (≤ 15 cm) tends to reduce the diameter of the nanoparticles due to the increase in the strength of the electric field (Ibili and Dasdemir 2019; Niu et al. 2020). Distances above 6 cm are recommended, as they ensure total evaporation of the solvent and stability of the Taylor cone, generating homogeneous spherical nanoparticles (Ibili and Dasdemir 2019; Niu et al. 2020).

The main environmental conditions that need to be controlled during the electrospraying technique correspond to relative humidity and ambient temperature. Moderate relative humidity contributes to the absorption of water vapor on the surface of the drop at the tip of the capillary. In the path between the capillary and the collector, the water evaporates along with the solvent, providing the formation of pores on the surface of the nanoparticles. In this way, high relative humidity is not recommended, as it can influence the solvent volatilization producing wet nanoparticles or results in the dripping of the polymeric solution (Niu et al. 2020).

For the production of nanoparticles by the electrospraying technique temperature of approximately 20°C is generally used. The increase in the temperature can accelerate the molecular interactions in the polymeric solution and the evaporation rate of the solvent, besides reducing the viscosity and surface tension of the polymeric solution drop at the capillary tip. These alterations contribute to the reduction of the nanoparticle diameter. However, they can make the technique unfeasible since non-viscous polymeric solutions impair nanomaterials development. Thus, temperature control is essential to obtain nanoparticles with the desired characteristics (Niu et al. 2020).

6. Methodologies For The Characterization Of Gas Adsorbent Nanoparticles

The properties of the nanoparticles, such as chemical, electronic, optical, and mechanical properties can differ significantly from particles with a macro scale, due to the greater reactivity at the molecular level in function to the high surface-volume ratio. Therefore, to obtain more information about the properties and potential applications of these nanostructures, their characterization is essential. The nanoparticles can be characterized in terms of morphology, size, surface area, porosity, elemental composition, crystalline structure, adsorption potential, surface charge, and various other physical properties (Mourdikoudis et al. 2018).

Several techniques are applied to characterize nanoparticles (Fig. 3), among them the most used are: scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS, EDX or XEDS), Fourier transform infrared spectroscopy (FTIR), dynamic light scattering (DLS), Zeta potential, Brunauer-Emmett-Teller method (BET), Barret-Joyner-Halenda method (BJH), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Campos et al. 2015).

The most important parameters in the characterization of nanoparticles are the size and morphology. SEM and TEM are the most used techniques to evaluate these parameters. The principle of electron microscopy is the use of accelerated electron beams and electrostatic or electromagnetic lenses to generate images with high resolution, based on the electron wavelengths (Crucho and Barros 2017). The images of TEM, compared to SEM, provide more precise information about the size, shape, and crystallography of the nanoparticles due to the greater magnification and resolution obtained in this technique.

Techniques based on electron microscopy require careful sample preparation, which involves chemical fixation, staining, chemical dehydration, incorporation, critical point drying, cutting in thin sections, cryofixation or incorporation, and coating. However, the sample preparation for SEM is less demanding than for TEM. In the SEM, the samples are fixed on metallic support with double carbon adhesive tape and spray-coated with gold or carbon to make the sample conductive and increase the contrast of the image (De la Calle et al. 2016). The sample preparation for TEM is more complex and time-consuming because it usually requires cuts in ultrafine sections to allow the transmission of electrons. The thin films containing the samples are prepared on copper grids coated with carbon. For this, the solution sample is deposited on the grid, and the excess is removed with absorbent paper.

EDS (or EDX or XEDS) is used for the elemental analysis or chemical characterization of the nanomaterial. This technique is applied together with SEM or TEM and it is based on the interaction of some source of X-ray excitation and a sample because each chemical element has a unique atomic structure which allows a unique set of peaks on its electromagnetic emission spectrum (Crucho and Barros 2017). FTIR is a chemical analysis technique used to identify surface the functional groups present in the nanoparticles. FTIR measures the absorption intensity of the infrared light as a function of the wavelength of the light (Campos et al. 2015).

DLS and zeta potential determine the size distribution and surface charge of nanoparticles, respectively. In the DLS, the colloidal suspension of spherical particles is illuminated by a beam of monochromatic light (laser) directed to the photon detector. The light intensity disperses over time due to the Brownian motion of that is related to the equivalent hydrodynamic diameter of particles. This diameter is determined from an autocorrelation function. The DLS provides information about all the particles quickly, being one of the advantages of this technique (Crucho and Barros 2017).

The Zeta potential is an important indicator of the surface charge of the nanoparticles. This technique can be used to predict and control the stability of colloidal suspensions or emulsions, and it is essential

for the understanding of dispersion and aggregation processes (Parhi and Suresh 2012). In addition, the surface hydrophobicity can be estimated by this technique. The value of ± 30 mV of the zeta potential is generally used to infer the stability of the particles. The absolute value above 30 mV indicates a stable condition, while below 30 mV indicates characteristics of instability, such as aggregation, coagulation, or flocculation (Sapsford et al. 2011).

The textural properties of the nanoparticles are generally determined by physical adsorption techniques, which are extremely important to evaluate the adsorption capacity of the nanoparticles. In these methods is used a surface analyzer that uses nitrogen (N_2) gas as an adsorbent and liquid N_2 (77 K) as a refrigerant medium, being the surface area obtained in the relative pressure range P/P_0 of 0.05 to 0.35 (Campos et al. 2015). To obtain the adsorption/desorption isotherms and the specific surface area is used the BET mathematical method. Size, shape, and distribution of the pores can be calculated from the isotherms by BJH mathematical model (Campos et al. 2015).

TGA and DSC can measure the thermal stability. TGA determines the thermal degradation according to the sample mass variation as a function of the temperature, and it allows evaluating if there is a residual solvent in the nanoparticles. DSC evaluates the physical-chemical state of the nanoparticles, determining the phase transitions, such as temperatures of glass transition (T_g), crystallization, and melting. T_g is the reversible transition that occurs in amorphous materials (including amorphous regions within semicrystalline polymers), where the material changes from a hard and relatively brittle state into a molten or rubber-like state (Crucho and Barros 2017).

For evaluation of hydrophobicity of the nanoparticles, the contact angle that the liquid (water drop) forms when deposited on the surface is measured. With a digital microscope, the interface between the water drop and the solid is photographed, and the angle is automatically determined (Dwivedi et al. 2017). To choose the most appropriate technique must know the strengths and limitations of all to know if the use of only one is sufficient to obtain reliable information about a specific parameter, or if a combination of techniques for characterizing of the nanoparticles is necessary (Mourdikoudis et al. 2018).

7. Co Adsorption Mechanism In Nanomaterials

Adsorption is an emerging alternative for capturing CO_2 , where it is possible to explore different types and structures of solids (Nocito and Dibenedetto 2020). Nanomaterials are promising adsorbents to overcome many limitations of these processes. They have relatively high CO_2 capture capabilities and are reusable over several adsorption/desorption cycles. Generally, nanomaterials require low energy for regeneration. The efficiency of the adsorption process depends: on the temperature and concentration of the adsorbed substance (adsorbate); aggregation state of the solid (adsorbent); as well as of the adsorbate and adsorbent natures; and the type of fluid that will contact them (Mansour et al. 2016). In the adsorption technique, the adsorbent is the most practical component of the system to make changes, to increase the CO_2 capture efficiency.

The material and the morphology of these nanostructures influence the gas adsorption process on the nanoparticle surface. The high surface area of the nanoparticles provides several adsorption sites (pores), where CO₂ can bind (Beltzung et al. 2018). Electrospinning (production of nanofibers) or electrospraying (production of nanoparticles) can produce structures with relatively high porosity. The reduction in diameter increases the specific surface area per volume unit and, consequently, provides more accessible adsorption sites for the compound to be adsorbed. The adsorption rate of the nanoparticles is proportional to the number of free pores on the adsorbent's surface (Bera and Belhaj 2016).

The choice of suitable polymer for the development of nanoparticles can be the differential in improving adsorption. The presence of functional groups containing nitrogen enables a favorable chemical interaction between polymeric matrix and CO₂, due to the improved surface polarity by acid-base and dipole-quadrupole interactions (Beltzung et al. 2018; Nocito and Dibenedetto 2020). Carbon nanofibers composed of the PAN polymer are advantageous in the adsorption of CO₂ compared to other polymers. The reversible link between the nitrogen functional groups to CO₂ that allows the subsequent desorption of the gas, in addition to guaranteeing structural resistance to thermal changes (Beltzung et al. 2018).

The rate of effective adsorption of the gas enhances with the increasing concentration of nanoparticles in the liquid medium. However, this occurs up to a maximum limit. This phenomenon is known as Brownian motion, which is the random displacement of particles in suspension. When the concentration of particles is high, reaching a critical value, Brownian motion is reduced, as the interaction between them makes it difficult to move (Nagarajan 2008). Asmaly et al. (2015) developed carbon nanofibers with 1% of NPsFe₂O₃ to remove phenol ions from water. Almost 100% of phenol removal was obtained with 200 mg of nanofiber with NPsFe₂O₃. There was an increase in the phenol removal efficiency with the increase in dosage to 400 mg. The authors observed at higher concentrations of the nanofiber, there was a reduction in adsorption due to the overlap of active sites. Consequently, this reduces the binding sites for the adsorption of molecules. However, the results with 200 mg showed the excellent removal efficiency of phenol by nanofiber even at lower adsorbent dosage.

According to the Langmuir model, the adsorption of molecules in one site does not influence the adsorption in neighboring sites, which makes the process favorable and reversible (Chaúque et al. 2017). PAN nanofibers maintain the adsorption capacity for up to 3 cycles and reduce to 81.9% in the fourth cycle and the maximum removal of CO₂ from the nanostructure occurs at pH 5 (Vaz et al. 2019). Microalgae cultivation has an optimum pH for growth around 8–10 (Cardias et al. 2018). Therefore, the application of this process in microalgal cultivation (Fig. 4) would not be a hindrance, since the CO₂ injected into the cultivation reacts with water and forms carbonic acid that allows the gas desorption by nanomaterial (Vaz et al. 2019). Nanostructures may have a higher adsorption capacity than popular adsorbents, such as activated carbon and zeolites, mainly due to the number and size of pores. Other materials, such as microporous organic polymers, may present a higher CO₂ capture capacity. However,

the synthesis of these compounds is expensive and complex (Beltzung et al. 2018). Thus, polymeric nanoparticles can be an adequate and efficient alternative to act in the CO₂ adsorption process.

8. Nanobiotechnology As An Alternative For Co2 Mitigation And Future Perspectives

The CO₂ is the main polluting gas in the environment, and the increase of its emissions to the atmosphere is responsible for the greenhouse effect phenomenon and consequent global warming of the planet. Several studies are in progress to provide productive and viable solutions for the processing and/or use of this gas, to reduce its concentration in the atmosphere. CO₂ sequestration techniques developed worldwide use microalgae to gas biofixation through the process of photosynthesis (Agarwal et al. 2019).

The demand for innovative technologies into useful materials for the biological study is based on two technologies: biotechnology and nanotechnology. Nanotechnology is a science that involves materials and equipment capable of modifying physical and chemical properties of substances in molecular dimensions. Biotechnology uses the knowledge and biology techniques to manipulate the physiological processes of biological individuals (Fakruddin et al. 2012). The interactions between cells and nanomaterials reveal the potential of nanobiotechnology to promote new methodologies for the large-scale production of microalgae biomass.

Several works were performed to mitigate CO₂ through chemical and/or biological biofixation by microalgae. In a pioneering study, Vaz et al. (2019) developed polymeric nanofibers for physical adsorption of CO₂ in the cultivation of microalga. The authors cultivated the microalga *Chlorella fusca* LEB 111 with PAN nanofibers, and they observed an increase of the CO₂ biofixation by microalga, as well as higher biomass production.

Moreover, to increase CO₂ biofixation in the cultivation of microalgae, studies were carried out with the addition of NPsFe₂O₃ in the PAN nanofibers. The nanoparticles increased the specific surface area and porosity of the nanofibers, and these characteristics are essential for the application of the nanostructures as adsorbent materials. Therefore, the authors confirmed that nanofibers containing NPsFe₂O₃ increased the adsorption and desorption capacity of the CO₂ in the cultivations and, consequently, the gas biofixation by microalgae (Vaz et al. 2019, 2020). These innovative researches integrate nanotechnology and biotechnology, based on the longer contact time between the CO₂ and the microorganism. In general, gas injected into the cultivations permeates through the liquid column and quickly escapes into the atmosphere, not being fully absorbed by the microalgae. Thus, with the addition of the adsorbent nanostructures in the cultivations, the CO₂ adsorption occurs, keeping it available for the microalgae for a longer time, which allows greater gas biofixation (Vaz et al. 2020).

Compared with polymeric nanofibers, PAN nanoparticles have higher CO₂ mitigation potential due to their smaller diameter and, consequently, greater specific surface area with adsorption sites available to capture the gas and keep it for longer in the microalgal cultivation. In addition to CO₂ adsorption, the microalgal biomass also adsorbs on these nanostructures. This adsorption capacity can favor the biomass harvest at the end of the production. The advantages of using nanoparticles, concerning the traditional harvesting, are low energy consumption, rapid separation of the biomass, the possibility of reuse of the nanoparticles, and reducing the cost of the microalgae harvesting process, which generally constitutes 20 to 30% of the total cost (Duman et al. 2019).

Nanobiotechnology can reduce the CO₂ emissions, directly and indirectly, through the development of biodegradable packaging with the polymer polyhydroxybutyrate (PHB) extracted from the microalgae biomass. Biodegradable polymers do not have good mechanical and barrier properties. However, carbon nanotubes (CNTs) or cellulose nanocrystals can increase these properties, allowing the application of biopolymers in the packaging area (Durán and Marcato 2013). According to Morais et al. (2016), the microalgal PHB can be applied as a coating material in the nanoencapsulation of bioactive compounds. Nanocapsules produced from biopolymers can provide a chemical and physical barrier against radicals, oxygen, or ultraviolet radiation.

In this perspective, the application of nanobiotechnology in the mitigation of CO₂ by microalgae involves: the development of new nanomaterials that are capable of increasing the gas biofixation by microorganisms; reduce the main polluting gas of the environment; reduce costs with a carbon source for the production of microalgal biomass, and make viable the increase of scale for the production of microalgae biomass with potential applications in several areas (Fakruddin et al. 2012).

The main challenges of the nanobiotechnology involve evaluating the risks of the nanomaterials to human health and the environment, to prevent any adverse consequences. This evaluation consists in to develop applicable methods and/or instruments able to evaluate the toxicity and/or exposure to the nanomaterials (Fakruddin et al. 2012). Furthermore, environmental, health, and safety issues of the nanomaterials have a strong influence on the acceptance of nanotechnology by the public and, consequently, affect their sustainability.

9. Conclusions

Polymeric nanoparticles produced by electrospraying are potential adsorbents that can be used to the CO₂ capture due to the gas adsorption capacity for these materials. The application of adsorbent nanoparticles produced by electrospraying in microalgal cultivation is a recent and promising technology, with the potential to maximize the efficiency of CO₂ biofixation by microalgae and reduce the harmful effects of this gas to the environment. Thus, the implementation of nanobiotechnology in this scenario aims at a sustainable increase in culture's productivity, as well as representing a valuable advance to achieve social and economic sustainability.

Declarations

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) - Brazil - Finance Code 001. The authors also thank the MCTIC (Ministry of Science Technology, Innovation and Communication).

Conflicts of interest/Competing interests: Not applicable.

Availability of data and material (data transparency): Not applicable.

Code availability (software application or custom code): Not applicable.

Authors' contributions: M.G. Moraes: Conceptualization, Writing - review & editing, Supervision. B. P. Vargas: Conceptualization, Investigation, Writing - original draft. B.S. Vaz: Conceptualization, Investigation, Writing - original draft. B.B. Cardias: Conceptualization, Investigation, Writing - original draft. J.A.V. Costa: Conceptualization, Writing - review & editing, Supervision.

References

1. Abdolahi-Mansoorkhani H, Seddighi S (2019) H₂S and CO₂ capture from gaseous fuels using nanoparticle membrane. *Energy* 168:847-857. <https://doi.org/10.1016/j.energy.2018.11.117>
2. Acién FG, Fernández JM, Magán JJ, Molina E (2012) Production cost of a real microalgae production plant and strategies to reduce it. *Biotechnol Adv* 30:1344-1353. <https://doi.org/10.1016/j.biotechadv.2012.02.005>
3. Agarwal P, Gupta R, Agarwal N (2019) Advances in Synthesis and Applications of Microalgal Nanoparticles for Wastewater Treatment. *J Nanotechnol* 2019:1-9. <https://doi.org/10.1155/2019/7392713>
4. Ali M, Al-Anssari S, Arif M, Barifcani A, Sarmadivaleh M, Stalker L, Lebedev M, Iglauder S (2019) Organic acid concentration thresholds for ageing of carbonate minerals: Implications for CO₂ trapping/storage. *J Colloid Interface Sci* 534:88-94. <https://doi.org/10.1016/j.jcis.2018.08.106>
5. Aresta M, Dibenedetto A, Angelini A (2013) The changing paradigm in CO₂ utilization. *J CO₂ Util* 3-4:65-73. <https://doi.org/10.1016/j.jcou.2013.08.001>
6. Asmaly HA, Abussaud B, Ihsanullah, Saleh TA, Gupta VK, Atieh MA (2015) Ferric oxide nanoparticles decorated carbon nanotubes and carbon nanofibers: From synthesis to enhanced removal of phenol. *J Saudi Chem Soc* 19:511-520. <https://doi.org/10.1016/j.jscs.2015.06.002>
7. Beltzung A, Klaue A, Colombo C, Wu H, Storti G, Morbidelli M (2018) Polyacrylonitrile Nanoparticle-Derived Hierarchical Structure for CO₂ Capture. *Energy Technol* 6:718-727. <https://doi.org/10.1002/ente.201700649>

8. Bera A, Belhaj H (2016) Application of nanotechnology by means of nanoparticles and nanodispersions in oil recovery - A comprehensive review. J Nat Gas Sci Eng 34:1284-1309. <https://doi.org/10.1016/j.jngse.2016.08.023>
9. Bock N, Dargaville TR, Woodruff MA (2012) Electro spraying of polymers with therapeutic molecules: state of the art. Prog Polym Sci 37:1510-1551. <https://doi.org/10.1016/j.progpolymsci.2012.03.002>
10. Campos EA, Pinto DVBS, Oliveira JISD, Mattos EDC, Dutra RDCL (2015) Synthesis, characterization and applications of iron oxide nanoparticles-a short review. J Aerosp Technol Manag 7:267-276. <https://doi.org/10.5028/jatm.v7i3.471>
11. Cardias BB, Morais MG, Costa JAV (2018) CO₂ conversion by the integration of biological and chemical methods: *Spirulina* sp. LEB 18 cultivation with diethanolamine and potassium carbonate addition. Bioresour Technol 267:77-83. <https://doi.org/10.1016/j.biortech.2018.07.031>
12. Chaúque EFC, Dlamini LN, Adelodun AA, Greyling CJ, Ngila JC (2017) Electrospun polyacrylonitrile nanofibers functionalized with EDTA for adsorption of ionic dyes. Phys Chem Earth 100:201-211. <https://doi.org/10.1016/j.pce.2016.10.008>
13. Comitre AA, Vaz BS, Costa JAV, Morais MG (2021) Renewal of nanofibers in *Chorella fusca* microalgae cultivation to increase CO₂ fixation. Bioresour Technol 321:124452. <https://doi.org/10.1016/j.biortech.2020.124452>
14. Crucho CI, Barros MT (2017) Polymeric nanoparticles: A study on the preparation variables and characterization methods. Mater Sci Eng C 80:771-784. <https://doi.org/10.1016/j.msec.2017.06.004>
15. De la Calle I, Menta M, Séby F (2016) Current trends and challenges in sample preparation for metallic nanoparticles analysis in daily products and environmental samples: a review. Spectrochim Acta Part B 125:66-96. <https://doi.org/10.1016/j.sab.2016.09.007>
16. Duman F, Sahin U, Atabani AE (2019) Harvesting of blooming microalgae using green synthesized magnetic maghemite (γ -Fe₂O₃) nanoparticles for biofuel production. Fuel 256:115935. <https://doi.org/10.1016/j.fuel.2019.115935>
17. Durán N, Marcato PD (2013) Nanobiotechnology perspectives. Role of nanotechnology in the food industry: a review. Int J Food Sci 48:1127-1134. <https://doi.org/10.1111/ijfs.12027>
18. Dwivedi C, Pandey I, Pandey H, Ramteke PW, Pandey AC, Mishra SB, Patil S (2017) Electrospun nanofibrous scaffold as a potential carrier of antimicrobial therapeutics for diabetic wound healing and tissue regeneration. In: Grumezescu AM (ed) Nano- and microscale drug delivery systems, Elsevier, Amsterdam, pp 147-164
19. Fakruddin M, Hossain Z, Afroz H (2012) Prospects and applications of nanobiotechnology: a medical perspective. J Nanobiotechnology 10:1-8. <https://doi.org/10.1186/1477-3155-10-31>
20. Ibili H, Dasdemir M (2019) Investigation of electrohydrodynamic atomization (electro spraying) parameters' effect on formation of poly (lactic acid) nanoparticles. J Mater Sci 54:14609-14623. <https://doi.org/10.1007/s10853-019-03899-6>

21. IEA – International Energy Agency (2019) Global Energy Review 2019.
<https://www.iea.org/reports/global-energy-review-2019>. Accessed 18 september 2020
22. Ikedi CU (2018) Economic Impact of CO₂ Mitigation Devices in Sustainable Buildings. In: Silva V (ed) Low Carbon Transition: Technical, Economic and Policy Assessment, IntechOpen, United Kingdom, pp 73-88
23. Jeevanandam J, Barhoum A, Chan YS, Dufresne A, Danquah MK (2018) Review on nanoparticles and nanostructured materials: History, sources, toxicity and regulations. Beilstein J Nanotechnol 9:1050-1074. <https://doi.org/10.3762/bjnano.9.98>
24. Khan I, Saeed K, Khan I (2019) Nanoparticles: Properties, applications and toxicities. Arab J Chem 12:908-931. <https://doi.org/10.1016/j.arabjc.2017.05.011>
25. Koronaki IP, Prentza L, Papaefthimiou V (2015) Modeling of CO₂ capture via chemical absorption processes - An extensive literature review. Renew Sustain Energy Rev 50:547-566.
<https://doi.org/10.1016/j.rser.2015.04.124>
26. Lam MK, Lee KT, Mohamed AR (2012) Current status and challenges on microalgae-based carbon capture. Int J Greenh Gas Control 10:456-469. <https://doi.org/10.1016/j.ijggc.2012.07.010>
27. Leung DY, Caramanna G, Maroto-Valer MM (2014) An overview of current status of carbon dioxide capture and storage technologies. Renew Sustain Energy Rev 39:426-443.
<https://doi.org/10.1016/j.rser.2014.07.093>
28. Li S, Pyrzyński TJ, Klinghoffer NB, Tamale T, Zhong Y, Aderhold JL, James Zhou S, Meyer HS, Ding Y, Bikson B (2017) Scale-up of PEEK hollow fiber membrane contactor for post-combustion CO₂ capture. J Memb Sci 527:92-101. <https://doi.org/10.1016/j.memsci.2017.01.014>
29. Luis P (2016) Use of monoethanolamine (MEA) for CO₂ capture in a global scenario: Consequences and alternatives. Desalination 380:93-99. <https://doi.org/10.1016/j.desal.2015.08.004>
30. Mansour BR, Habib MA, Bamidele OE, Basha M, Qasem NAA, Peedikakkal A, Laoui T, Ali M (2016) Carbon capture by physical adsorption: Materials, experimental investigations and numerical modeling and simulations - A review. Appl Energy 161:225-255.
<https://doi.org/10.1016/j.apenergy.2015.10.011>
31. Morais MG, Morais EG, Vaz BS, Gonçalves CF, Lisboa C, Costa JAV (2016) Nanoencapsulation of the bioactive compounds of *Spirulina* with a microalgal biopolymer coating. J Nanosci Nanotechnol 16:81-91. <https://doi.org/10.1166/jnn.2016.10899>
32. Mourdikoudis S, Pallares RM, Thanh NT (2018) Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties. Nanoscale 10:12871-12934. <https://doi.org/10.1039/C8NR02278J>
33. Nagarajan R (2008) Nanoparticles: Building blocks for nanotechnology. In: Nagarajan R, Hatton TA (eds) Nanoparticles: synthesis, stabilization, passivation and functionalization, American Chemical Society, Washington, pp 2-14

34. Ng LY, Mohammad AW, Leo CP, Hilal N (2013) Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review. *Desalination* 308:15-33.
<https://doi.org/10.1016/j.desal.2010.11.033>
35. Nguyen MK, Moon JY, Bui VKH, Oh YK, Lee YC (2019) Recent advanced applications of nanomaterials in microalgae biorefinery. *Algal Res* 41:101522.
<https://doi.org/10.1016/j.algal.2019.101522>
36. Niu B, Shao P, Luo Y, Sun P (2020) Recent advances of electrosprayed particles as encapsulation systems of bioactives for food application. *Food Hydrocoll* 99:105376.
<https://doi.org/10.1016/j.foodhyd.2019.105376>
37. Nocito F, Dibenedetto A (2020) Atmospheric CO₂ mitigation technologies: carbon capture utilization and storage. *Curr Opin Green Sustain Chem* 21:34-43. <https://doi.org/10.1016/j.cogsc.2019.10.002>
38. Parhi R, Suresh P (2012) Preparation and characterization of solid lipid nanoparticles-a review. *Curr Drug Discov Technol* 9:2-16. <https://doi.org/10.2174/157016312799304552>
39. Park CH, Lee J (2009) Electrosprayed polymer particles: effect of the solvent properties. *J Appl Polym Sci* 114:430-437. <https://doi.org/10.1002/app.30498>
40. Petrík S (2011) Industrial production technology for nanofibers. Nanofibers–production, properties and functional applications. In: Lin T (ed) *Nanofibers: Production, Properties and Functional Applications*, IntechOpen, United Kingdom, pp 3-16
41. Rahaman MSA, Cheng LH, Xu XH, Zhang L, Chen HL (2011) A review of carbon dioxide capture and utilization by membrane integrated microalgal cultivation processes. *Renew Sustain Energy Rev* 15:4002-4012. <https://doi.org/10.1016/j.rser.2011.07.031>
42. Rosa GM, Morais MG, Costa JAV (2018) Green alga cultivation with monoethanolamine: Evaluation of CO₂ fixation and macromolecule production. *Bioresour Technol* 261:206-212.
<https://doi.org/10.1016/j.biortech.2018.04.007>
43. Sapsford KE, Tyner KM, Dair BJ, Deschamps JR, Medintz IL (2011) Analyzing nanomaterial bioconjugates: a review of current and emerging purification and characterization techniques. *Anal Chem* 83:4453-4488. <https://doi.org/10.1021/ac200853a>
44. Vaz BS, Costa JAV, Morais MG (2019) Innovative nanofiber technology to improve carbon dioxide biofixation in microalgae cultivation. *Bioresour Technol* 273:592-598. doi:
<https://doi.org/10.1016/j.biortech.2018.11.054>
45. Vaz BS, Costa JAV, Morais MG (2020) Physical and biological fixation of CO₂ with polymeric nanofibers in outdoor cultivations of *Chlorella fusca* LEB 111. *Int J Biol Macromol* 151:1332-1339.
<https://doi.org/10.1016/j.ijbiomac.2019.10.179>
46. Zainab G, Babar AA, Iqbal N, Wang X, Yu J, Ding B (2018) Amine-impregnated porous nanofiber membranes for CO₂ capture. *Compos Commun* 10:45-51.
<https://doi.org/10.1016/j.coco.2018.06.005>

47. Zhang Y, Guan J, Wang X, Yu J, Ding B (2017) Balsam-Pear-Skin-Like Porous Polyacrylonitrile Nanofibrous Membranes Grafted with Polyethyleneimine for Postcombustion CO₂ Capture. ACS Appl Mater Interfaces 9:41087-41098. <https://doi.org/10.1021/acsami.7b14635>

Figures

Figure 1

Schematic illustration of CO₂ mitigation technologies

Figure 2

Schematic diagram of the electrospraying technique

Figure 3

Illustrative representation of the techniques applied in the characterization of the nanoparticles

Figure 4

Process of CO₂ adsorption/desorption by nanoparticles in microalgae cultivation

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [OnlineMoraisetalgraphicalabstract.png](#)