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Elucidating the role of nanoparticles on photosynthetic biogas upgrading: Influence of biogas type, nanoparticle concentration and light source

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Abstract

Three different nanoparticles, namely Fe$_2$O$_3$, carbon coated zero valent iron (CACOI) and SiO$_2$, were added to a mixed microalgae culture in order to improve photosynthetic biogas upgrading. Fe$_2$O$_3$ and CACOI nanoparticles at 10 mg/L supported higher CO$_2$ consumptions compared to their respective controls. The addition of Fe$_2$O$_3$ nanoparticles at 70 mg/L resulted in a 38% enhanced biomass productivity, and 20% higher CO$_2$ consumption but delayed exponential growth. The CACOI nanoparticles at 70 mg/L resulted in a shorter lag phase, enhanced CO$_2$ consumption by 13%, and carbohydrate content enhancement by 64%, while the addition of SiO$_2$ nanoparticles at this concentration induced an enhanced lipid and carbohydrates production by 47% and 68%, respectively. Interestingly, UV light exposure reduced the beneficial effects of nanoparticles, although CACOI nanoparticles still supported a shorter lag phase and higher carbohydrates production at 70 mg/L. In brief, CACOI nanoparticles hold an untapped potential to promote the metabolism of microalgae during photosynthetic biogas upgrading.

**Keywords:** biogas upgrading, biomass productivity, nanoparticles, microalgae, optimization, UV exposure

**Abbreviations**

*BA* biogas A

*BB* biogas B

*BET* Brunauer–Emmett–Teller

*BJH* Barrett, Joyner & Halenda

*CACOI* Carbon coated zero valent iron
1. Introduction

Biogas has become a relevant renewable energy source with the potential to substitute natural gas in the context of the World’s Ecological Transition. Biogas is typically produced via anaerobic digestion of organic matter and its composition varies depending on the redox state of the substrates, environmental and operational conditions in the digesters. This green gas vector is mainly composed of CH$_4$ (45-75%), CO$_2$ (25-55%) and H$_2$S (0.005-2%) [1]. In this context, the removal of contaminants such as CO$_2$ and H$_2$S is
mandatory prior to its use as a vehicle fuel or to its injection to the natural gas grid [2].

Today, several physical and chemical methods are commercially available for biogas upgrading, including membrane separation, cryogenic separation, pressure swing adsorption, water scrubbing, organic solvent scrubbing, chemical absorption [3]. The high operating costs and environmental impacts of these physical/chemical technologies have triggered research in biological methods such hydrogenotrophic and photosynthetic biogas upgrading.

Photosynthetic biogas upgrading in microalgae-bacteria photobioreactors has been validated at pilot and demo-scale, and widely reported to be an economically and environmentally friendly option to upgrade biogas into biomethane coupled to nutrient recovery from the liquid fraction of digestates [4]. Despite algal-bacterial photobioreactors interconnected to external biogas absorption columns have reached CO₂ removals of up to 98.6% at pilot [5] and demo scale [4], there are still some challenges that need to be addressed to maintain a robust biogas upgrading performance. Recently, Bose et al [6] compared seven different factors affecting the bubble column performance in photosynthetic biogas upgrading. The main process limitations identified to date are i) the low CO₂ mass transfer to the culture medium, ii) the high sensitivity of biomethane quality to variations in the gas and liquid flow rates and pH, and iii) the diurnal and seasonal variability of environmental parameters influencing photosynthetic activity [7]. Indeed, this process requires the development of innovative operational strategies to enhance CO₂ absorption and fixation.

During the past years, the use of nanomaterials in environmental applications is gaining attention due to their unique physicochemical properties such as size, morphology, high reactivity, chemical stabilization, high surface area-to-volume ratio, abundant active
sites and high adsorption capacity [8]. Indeed, nanomaterials and nanoparticles can play an key role in CO₂ capture technologies, biogas production and biogas upgrading processes [9]. To date, many solid adsorbents, mainly porous materials, have been effectively used to remove CO₂ from biogas, such as activated carbons and metal oxides [10]. Moreover, it is known that the use of metal oxide NPs mediates the formation of carbonates, bicarbonates and carboxylates when CO₂ interacts with the NPs surfaces [11]. In this context, the addition of nanoporous materials to microalgae cultures devoted to biogas upgrading can create a symbiosis where the materials adsorb CO₂ to form carbonates and bicarbonate species that can be further fixed via photosynthesis by microalgae. This would result in enhancements in biomass production and in the performance of biogas purification. In addition, it has been recently demonstrated that the supplementation of graphene oxide quantum dots under UV-light exposure stimulated the CO₂ capture and lipid production in Chlorella pyrenoidosa [12]. Thus, NPs can be also used as a strategy to scavenge the damage of solar UV radiation to microalgae.

The addition of metal oxide NPs to microalgae culture is still a controversial topic, since NPs can be toxic to some microalgae species or stimulate their growth and lipid production (Table 1). Even if there is very little information on how the NPs addition to microalgae culture can improve the CO₂ adsorption, the reported studies present promising results [13]. In this way, the physico-chemical properties of the NPs can represent an advantage to improve CO2 adsorption since they can act as electron donors/acceptors and light conversion aids, or form carbonates when CO₂ interacts with their surface, among others. Jeon et al. [14] reported that SiO₂ NPs enhanced the gas-liquid mass transfer rate of CO₂ in C. vulgaris cultures, resulting in an enhanced growth and lipid production. Similarly, the use of polymeric nanofibers containing Fe₂O₃ NPs has been reported as a
promising technique to enhance CO$_2$ fixation of *Chlorella fusca* LEB 111 cultures [13]. On the other hand, the addition of zero-valent iron NPs have proved to have beneficial effects on microalgae species like *Pavlova lutheri*, *Isochrysis galbana*, *Tetraselmis suecica*, [15] *Desmodesmus subcapicatus*, *Dunaliella salina*, *Parachlorella kessleri* and *Trachydiscus minutus* [16]. However, to the best of our knowledge, little is known about the effect of carbon NPs on microalgae culture. The literature on the effect of carbon-coated zero-valent iron NPs on microalgae and the number studies devoted to investigate the potential of NPs during photosynthetic biogas upgrading is scarce.

This study aimed at assessing the effect of two metal oxides NPs (Fe$_2$O$_3$ and SiO$_2$) and one magnetic NP (carbon coated zero-valent iron) on microalgae growth and photosynthetic biogas upgrading efficiency at laboratory scale in batch enclosed photobioreactors. Additionally, the influence of NPs concentration and light source (visible versus visible+UV) on the parameters above mentioned were also investigated.

Table 1. Effect of nanoparticles on microalgae growth. PAN: polyacrylonitrile; DMF: dimethylformamide (DMF); NFs: nanofibers.

| NP            | Strain            | CO$_2$ source | Effect                                                                 | Reference |
|---------------|-------------------|---------------|------------------------------------------------------------------------|-----------|
| Fe$_2$O$_3$   | *Chlorella vulgaris* | CO$_2$ gas    | At concentrations of 50 and 100 mg/L biomass growth was reduced by 41.2% and 83.7% whereas total lipid contents increased by 39.7% and 25.5% respectively. | [17]      |
| g-C$_3$N$_4$  | *Scenedesmus sp.* |               | Improved biomass and lipid accumulation                                | [18]      |
| PAN/DMF NFs   | *Chlorella fusca* LEB | 15% v/v CO$_2$ gas | Assays with 0.3 g/L nanofibers supported 10.9% greater lipid production than the assays | [13]      |
| Fe$_2$O$_3$ NPs | 111              |               |                                                                        |           |
without nanofiber

| Nanoparticle | Species | Effect |
|--------------|---------|--------|
| SiC          | Scenedesmus sp. | Improved biomass and lipid accumulation |
| TiC          |                     | Inhibitory effect |
| TiO₂         | Dunaliella tertiolecta | No evidence of NPs mediated inhibition of the growth or pigment content at concentrations up to 10 mg/L |
| ZnO          | Dunaliella tertiolecta | Growth was reduced at concentration of 1 mg/L |
| ZnO          | Skeletonema costatum | Growth was inhibited at 0.5 mg/L |
| ZVI          | Arthrospira maxima | Growth and lipid accumulation were stimulated at concentrations between 1.7-5.1 mg/L |
|             | Desmodesmus subspicatus |                     |
|             | Dunaliella salina |                     |
|             | Nannochloropsis limnetica |                     |
|             | Parachlorella kessleri |                     |
|             | Raphidocelis subcapitata |                     |
|             | Trachydiscus minutus |                     |
|             | Isochrysis galbana | Preference to nanoparticles over EDTA-Fe |
| ZVI          | Pavlova lutheri | Increase in lipid content |
|             | Tetraselmis suecica | Increased total cellular lipid content |

2. Materials and methods

2.1 Nanoparticles and stock solutions
Three different metal nanoparticles were investigated. Fe$_2$O$_3$ NPs were synthesized according to [22], while SiO$_2$ nanopowder was purchased from Sigma Aldrich. The CACOI nanoparticles were kindly donated by CALPECH. Fresh stock solutions of 200 mg/L of each nanoparticle were prepared in microalgae mineral medium, and sonicated for one hour to prevent nanoparticle agglomeration and facilitate the addition of the NPs to the microalgae culture. To determine the surface area, pore volume and average pore diameter of the NPs herein used, a nitrogen physisorption analysis was conducted in an ASAP 2050 (Micromeritics, USA) at 77 K. The specific surface area and pore characteristics were determined by the BET method and BJH equation. Scanning electron microscopy (SEM) (JEOL JSM-6490LV) and energy-dispersive spectroscopy (EDS) (EDX-700/800, Hitachi, Japan) were carried out to determine the surface morphology and elemental composition of the target NPs.

2.2 Microalgae culture and biogas

The microalgae culture used in our study consisted of a consortium of microalgae and cyanobacteria composed of Chlorella sp. (91.30 %), Nitzschia sp. (7.56 %) and Pseudanabaena sp (1.16 %) (percentages expressed in number of cells). The consortium was obtained from an outdoors 180 L pilot experimental plant treating real biogas and digestate from a 100 L sewage sludge digester located at the Institute of Sustainable Processes (Valladolid, Spain). The detailed description of the pilot plant can be found elsewhere [23,24]. To elucidate the effect of NPs on photosynthetic biogas upgrading, two different synthetic biogas mixtures were used: Biogas A composed of CO$_2$ (30%) and CH$_4$ (70%) (Carburos Metalicos; Spain), and Biogas B composed of CO$_2$ (29.5%), H$_2$S (0.5%) and CH$_4$ (70%) (Abello Linde; Spain).
2.3 Experimental set-up

Batch assays to quantitatively evaluate the effect of the different nanoparticles at different concentrations and under different light sources on biogas upgrading by microalgae were conducted in 1.2 L glass bottles. The bottles were prepared with 1 L of synthetic biogas headspace and 0.2 L of working volume, which was composed of mineral salt medium rich in carbonates as described elsewhere [25] and the corresponding nanoparticle concentration. The bottles were closed with butyl septa and plastic caps, flushed with helium for 5 min and, subsequently, the corresponding synthetic biogas was flushed for 5 min using inlet and outlet needles to replace the helium headspace. After one hour of stabilization, the bottles were inoculated with the mixed algal culture at an initial concentration of 200 mg/L of TSS. Then, the bottles were incubated at 25 ºC under continuous magnetic stirring (300 rpm) to avoid microalgae sedimentation. Light intensity of 900 µE/m²s was continuously provided by visible LED lights.

This study was divided in three tests series. In the tests series I, four operational conditions were evaluated for each nanoparticle: 1) Microalgae biomass and synthetic biogas A; 2) Microalgae biomass with 10 mg/L of nanoparticles and biogas A; 3) Microalgae biomass and synthetic biogas B; 4) Microalgae biomass with 10 mg/L of nanoparticles and biogas B. Each condition was run in triplicate. In tests series II, the influence of different concentrations (20, 40, and 70 mg/L) of each nanoparticle was assessed under biogas A headspace, 25 ºC, magnetic stirring (300 rpm) and visible light 900 µE/m²s. A control containing only algal biomass and biogas A was conducted. Each condition was run in triplicate. In test series III, the influence of different concentrations (20, 40, and 70 mg/L) of each nanoparticle was assessed under biogas A headspace, 25 ºC,
magnetic stirring (300 rpm) and visible light 900 μE/(m²s) + UV light (λ 315-350 nm, 10 W/m²). The UV light exposure was added to simulate real solar radiation. A control containing only algal biomass and biogas A was conducted. Each condition was run in triplicate.

### 2.4 Analytical procedures

The biogas composition in the headspace of the bottles was determined two times per day by gas chromatography-TCD (Bruker) to quantify the gas concentration of CH₄, CO₂, H₂S and O₂ in the headspace according to [26]. Microalgae growth was daily determined by optical density at 750 nm using a Shimadzu spectrophotometer (Japan), microalgae samples were daily taken and properly diluted to obtain an absorbance under 1, then the obtained absorbance was multiplied by the dilution factor. The initial CO₂ and O₂ content in the headspace along with the OD₇₅₀ were normalized and are presented as cumulative values. pH was determined at the beginning and at the end of the experiment (SensION™ + PH3 pHmeter, HACH, Spain). TSS concentrations were determined according to standard methods [27]. The biomass obtained from test series II and II was harvested (10000 rpm, 4 ºC) and freeze-dried for further macromolecular characterization. The carbohydrate content was determined according to [28], while the lipid content was determined gravimetrically following biomass extraction with chloroform:methanol (2:1 v/v) as described elsewhere [29].

### 2.5 Statistical analysis
The results are presented as mean values ± standard deviation. An analysis of variance (ANOVA) followed by Tuckey’s test considering α=0.05 was performed to assess the influence of nanoparticles on microalgae growth.

3. Results and discussion

3.1 Nanoparticle characterization

The SEM micrographs show the morphology of the three NPs used in this study (Fig. 1). The Fe$_2$O$_3$ NPs presented a nanorod morphology, which has been previously reported to exhibit a high specific surface area and better electrochemical and magnetic properties compared to other Fe$_2$O$_3$ morphologies [30]. The CACOI NPs were characterized by agglomerated NPs in accordance with [31]. Finally, the SiO$_2$ NPs presented the smallest particle size among the three NPs tested. Moreover, the chemical composition of each NPs is presented in Table 2. The presence of Na in the Fe$_2$O$_3$ NPs was attributed to trace levels of the catalyst used for their synthesis. Interestingly, the CACOI NPs exhibited low levels of essential minerals for microalgae growth, which could serve as nutrients and promote microalgae growth.

Table 2. Chemical composition of the different nanoparticles used. The values represent the atomic percentage. CACOI: carbon coated zero valent iron

| Element | Fe$_2$O$_3$ | CACOI | SiO$_2$ |
|---------|-------------|-------|---------|
| Si (%)  | 19.70       | 12.90 | 19.70   |
| O (%)   | 59.20       | 80.30 |         |
| Element | Na (%) | 3.44 |
|---------|--------|------|
| Fe (%)  | 37.40  | 1.74 |
| C (%)   | 85.10  |      |
| P (%)   | 0.09   |      |
| K (%)   | 0.23   |      |
| Ca (%)  | 0.03   |      |

**Fig. 1.** Scanning Electron Microscope micrographs of a) Fe₂O₃, b) CACOI; carbon coated zero valent iron, and c) SiO₂ nanoparticles.

Furthermore, the BET surface area, pore volume and average pore diameter of the target NPs are shown in Table 3. The three NPs herein used presented pore diameters <50 nm, and according to the IUPAC classification, the three NPs represent mesoporous materials. In this context, the NPs can serve as gas adsorbents and promote a higher CO₂
biofixation. It is known that Fe$_2$O$_3$ NPs represent an effective adsorbent of CO$_2$ [32], Hakim et al [33] reported that the CO$_2$ adsorption capacity of Fe$_2$O$_3$ increased up to four times when the particle size decreased from 160.5 nm (bulk form) to 24.5-56 nm. In our particular study, the synthesized Fe$_2$O$_3$ NPs exhibited an average particle size of 24 nm, which are in the range reported by [33]. Moreover, the morphology of the Fe$_2$O$_3$ NPs herein synthesized resulted in a higher BET surface area, which could eventually support a high CO$_2$ adsorption from biogas. On the other hand, the CACOI NPs presented slightly lower pore volume (0.28 cm$^3$/g), surface area (27.30 m$^2$/g) and average pore diameter (41.50 nm), than the Fe$_2$O$_3$ NPs, suggesting that both Fe$_2$O$_3$ and CACOI NPs can behave similarly as adsorbents. Finally, the SiO$_2$ NPs presented the highest BET surface area, pore volume and average pore diameter. The values obtained in our particular study ranged between the results reported by [34] and [35], suggesting that SiO$_2$ NPs could support superior adsorption properties than CACOI and Fe$_2$O$_3$ NPs. Thus, the results of the adsorption/desorption analysis confirmed that nanopowders exhibited a high surface area [36], but the nature of the CACOI and Fe$_2$O$_3$ NPs, inherently containing essential trace metals for microalgae growth, could play a key role in microalgae metabolism.

**Table 3.** BET surface area, pore volume and average pore diameter of the nanoparticles used in this study. BET: Brunauer-Emmett-Teller; CACOI: carbon coated iron

| Nanoparticles | BET surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Average pore diameter (nm) |
|---------------|-----------------------------|------------------------|---------------------------|
| Fe$_2$O$_3$   | 32.10                       | 0.38                   | 47.50                     |
| CACOI         | 27.30                       | 0.28                   | 41.50                     |
3.2 Influence of type of biogas and nanoparticle addition on microalgae growth

The CO₂ consumption and O₂ production recorded in the headspace of the bottles served as indicators of microalgae growth, along with the optical density of the culture broth (Fig. 2). The addition of biogas B resulted in microalgae inhibition regardless of the presence of NPs, and can be mainly attributed to the absence of sulfur-oxidizing bacteria responsible for the rapid oxidation of H₂S to SO₄²⁻ [37].
Fig. 2. Time course of the cumulative CO₂ consumption in the assays supplied with a) Fe₂O₃ NPs, b) CACOI NPs, c) SiO₂ NPs; cumulative O₂ production in the assays supplemented with d) Fe₂O₃ NPs, e) CACOI NPs, f) SiO₂ NPs; and culture absorbance of the algal consortium supplied with g) Fe₂O₃ NPs, h) CACOI NPs, i) SiO₂ NPs. NPs: nanoparticles; BA (triangles): assays with biogas A; BAN (circles): assays with biogas A and NPs; BB (diamonds): assays with biogas B; BBN (cross): assays with biogas B and NPs; CACOI: carbon coated zero valent iron.
On the other hand, biogas A did not induce microalgae inhibition likely due to the absence of H$_2$S. The cultures containing Fe$_2$O$_3$ NPs and SiO$_2$ NPs exhibited similar cumulative O$_2$ productions, CO$_2$ consumptions and culture densities than their controls (in the absence of NPs). Interestingly, Fe$_2$O$_3$ NPs have been previously reported as microalgal photosynthesis stimulants, resulting in enhancement in biomass growth and lipid/carbohydrate contents [38]. In our particular study, the addition of 10 mg/L of Fe$_2$O$_3$ NPs did not support any significant improvement in CO$_2$ cumulative consumptions but a slight enhancement of 5% in O$_2$ production was observed.

The addition of NPs at 10 mg/L did not enhance Px under biogas A atmosphere in any of the conditions tested. This can be attributed to the microalgae species used in this study, since the effect of the NPs is species specific (Table 4) [8]. Nonetheless, the microalgae cultivated with Fe$_2$O$_3$ NPs presented a statistically higher OD$_{750}$, likely supported by slightly higher O$_2$ production compared to the control tests. Indeed, the addition of 10 mg/L of Fe$_2$O$_3$ NPs stimulated the production of microalgal-bacterial biomass, which is in accordance with [38]. At this point it is important to mention that Xia et al [38] observed higher biomass growth enhancements at higher Fe$_2$O$_3$ NPs concentrations (50 mg/L), which suggested that the concentrations herein assessed were too low, and higher concentrations of Fe$_2$O$_3$ NPs can be added to observe an effect on photosynthetic biogas upgrading. Moreover, despite the addition of CACOI NPs resulted in a lower final OD$_{750}$ at the end of the experiment, the reduced lag phase in terms of O$_2$ production, CO$_2$ consumption and biomass growth suggested that CACOI NPs stimulated the activity of the algal consortium herein used. Even if little is known about the effect of CACOI NPs on microalgae, our results suggest that these particular NPs do not represent a threat for microalgae growth. Finally, the addition of 10 mg/L SiO$_2$ under a biogas A
atmosphere did not support any statistical difference in the monitored parameters compared to the control tests. SiO$_2$ NPs were previously reported as stimulants of *Chlorella vulgaris* metabolism, and final dry cell weight of 1.33 g/L were recorded by the addition of SiO$_2$ NPs [14]. Moreover, the same authors also observed that fatty acid methyl esters productivity was increased up to 0.62 g/L/day by the addition of the SiO$_2$ NPs. However, in our study no significant change was observed neither in the final dry weight nor in Px by the addition of SiO$_2$ NPs, probably because the study of Jeon et al. [14] used a concentration of 0.2 wt% SiO$_2$ NPs, which is much higher than the concentrations herein used. Thus, the absence of impact of SiO$_2$ NPs on algal metabolism compared to literature can be explained by the significant lower concentration herein used.

**Table 4.** Biomass productivity (Px) and pH of the algal consortium broth supplemented with 10 mg/L of the different nanoparticles. CACOI: carbon coated zero valent iron.

|            | Fe$_2$O$_3$ | CACOI | SiO$_2$ |
|------------|-------------|-------|---------|
|            | Control     | 10 mg/L | Control | 10 mg/L | Control | 10 mg/L |
| $P_x$ (g/L.d) | 0.78±0.005  | 0.77±0.07  | 1.30±0.07  | 1.29±0.032  | 1.32±0.03  | 1.38±0.06  |
| $pH_{initial}$ | 7.65±0.04  | 7.74±0.02  | 7.86±0.03  | 7.89±0.01  | 7.76±0.02  | 7.70±0.04  |
| $pH_{final}$ | 8.85±0.05  | 8.89±0.10  | 9.33±0.13  | 9.28±0.04  | 9.23±0.10  | 9.13±0.06  |

CACOI NPs are covered with carbon, and this particular material has been widely used for CO$_2$ capture [9]. The mechanism of interaction between the NPs and the CO$_2$ capture is not well understood yet, but one of the main mechanism of interaction is the “shuttle effect”, which can be described as follows: CO$_2$ is adsorbed by the NPs and then
the loaded NPs release the adsorbed CO$_2$ into the aqueous medium, or the algal broth in this case [39]. Thus, the reduced lag phase achieved in the presence of CACOI NPs could be explained by the adsorption capacity of activated carbon [31]. Hence, the CO$_2$ present in the biogas atmosphere was adsorbed to the surface of the NPs and rapidly released in the aqueous broth for microalgae consumption, thus stimulating an early algal metabolism.

### 3.3 Influence of nanoparticle concentration under visible light

The addition of 20, 40 and 70 mg/L of Fe$_2$O$_3$ NPs resulted in higher cumulative CO$_2$ consumption and higher Px during the exponential growth phase (Table 5) (Fig. 3). Indeed, the addition of Fe$_2$O$_3$ NPs resulted in up to 38% Px enhancement. The higher Px values herein obtained can be mainly attributed to: 1) the culture media composition, which is a synthetic centrate supporting high biomass productions due to its rich nutrients content compared to other types of wastewater [40]; 2) the high CO$_2$ concentration in the headspace of the bottle, which resulted in accelerated microalgal growth; 3) the biostimulant nature of the nanoparticles used and 4) the high photosynthetic active radiation and the high illuminated surface to volume ratio. However, the higher the Fe$_2$O$_3$ NPs concentration, the higher the lag phase in the assays (Fig 3a, d, g). This matched the observations of Bibi and co-workers [17], who reported that concentrations of Fe$_2$O$_3$ NPs between 50-100 mg/L delayed the exponential growth phase of microalgae. Although the cumulative CO$_2$ consumption and biomass productivity increased with increasing concentrations of Fe$_2$O$_3$ NPs, the cumulative O$_2$ production decreased as the NPs concentration increased. This phenomenon was likely due to the interactions between O$_2$ and Fe$_2$O$_3$ NPs via Fenton reactions, Photo-Fenton reactions, Haber-Weiss reactions or even more complex reactions [41], where the Fe$^{2+}$ ions released by the Fe$_2$O$_3$ NPs react with peroxide, water and O$_2$ to
form ROS. Even though the formation of ROS has been considered as one of the major factors that induce toxicity in microalgae [8], the use of Fe$_2$O$_3$ NPs presents contradictory results and the tolerance to Fe$_2$O$_3$ NPs is species specific. Thus, the retarded exponential phase could be attributed to the presence of ROS. Rana et al [42] reported that the biomass concentration of *Chlorella pyrenoidosa* was enhanced by 33.7% when 20 mg/L of Fe$_2$O$_3$ NPs were added, which is similar to the biomass enhancements obtained in our study.

**Table 5.** Biomass productivity (P$_x$) as a function of the type of nanoparticles and light source, at different concentrations. CACOI: carbon coated zero valent iron.

|          | Fe$_2$O$_3$ | CACOI | SiO$_2$ |
|----------|-------------|-------|---------|
|          | Visible light | Visible + UV light | Visible light | Visible + UV light | Visible light | Visible + UV light |
| Control  | 1.98±0.30    | 0.94±0.06  | 1.24±0.07 | 2.04±0.10  | 1.68±0.24  | 0.90±0.07  |
| 20 mg/L  | 1.44±0.18    | 1.45±0.13  | 1.69±0.48 | 2.00±0.14  | 1.89±0.08  | 0.88±0.05  |
| 40 mg/L  | 2.63±0.14    | 1.4±0.09   | 2.25±0.55 | 1.92±0.06  | 1.89±0.08  | 0.86±0.05  |
| 70 mg/L  | 2.75±0.23    | 1.8±0.15   | 3.12±0.65 | 2.14±0.03  | 1.81±0.13  | 0.85±0.08  |
Fig. 3. Time course of the cumulative CO₂ consumption in the assays supplied with different concentrations of a) Fe₂O₃ NPs, b) CACOI NPs, c) SiO₂ NPs; of the cumulative O₂ production in the tests supplemented with different concentrations of d) Fe₂O₃ NPs, e) CACOI NPs, f) SiO₂ NPs; and culture absorbance of the algal consortium supplied with different concentrations of g) Fe₂O₃ NPs, h) CACOI NPs, i) SiO₂ NPs. The assays were run under visible light. CACOI: carbon coated zero valent iron; NPs: nanoparticles.
The addition of Fe$_2$O$_3$ NPs did not enhance the carbohydrates or lipids content of the algal biomass (Fig. 4a) as previously reported by Bibi and co-workers [17]. However, these authors observed that the total lipid content of *C. vulgaris* depends on the time of exposure, and the long term exposure to high Fe$_2$O$_3$ NPs concentration resulted in a lipid degradation mediated by a defense mechanism of microalgae against ROS. Thus, the lower lipid content recorded in the assays containing 70 mg/L of Fe$_2$O$_3$ NPs is supported by the long term exposure to Fe$_2$O$_3$ and to the presence of ROS [17]. Finally, the results herein obtained suggests that Fe$_2$O$_3$ NPs acted as CO$_2$ adsorbents and increased CO$_2$ availability in the cultivation broth, a phenomenon which has been previously observed in a larger extent at increasing CO$_2$ concentrations [32]. However, the nature of Fe$_2$O$_3$ NPs to Fenton reactions and the formation of ROS interfered in the biomass production and macromolecular accumulation in the microalgae herein used.

**Fig. 4.** Influence of the concentration of a) Fe$_2$O$_3$ NPs; b) CACOI NPs; c) SiO$_2$ NPs on the carbohydrate (green) and lipid (blue) content of microalgae biomass at the end of the assays under visible light. CACOI: carbon coated zero valent iron; NPs: nanoparticles.
Compared to the assays with Fe$_2$O$_3$ NPs, the addition of CACOI NPs did not increase the lag phase of algal metabolism. Indeed, the addition of 70 mg/L of CACOI NPs enhanced both Px and the rates of CO$_2$ consumption, and reduced the lag phase (Fig. 3b, 3e, 3h). The cumulative CO$_2$ consumption in the 70 mg/L CACOI assays was 13% higher than in the control tests. The latter confirms the fact that CACOI NPs stimulated the CO$_2$ adsorption mainly by the nature of the material, and the increased CO$_2$ consumption could be mainly attributed to the higher CO$_2$ availability in the headspace of the bottles. Notwithstanding, the increasing concentrations of CACOI NPs did not impact significantly on the cumulative O$_2$ production and OD$_{750}$. However, the lag phase was significantly increased by the addition of the CACOI NPs, and was related to the increasing concentration. On the other hand, the carbohydrate content of the algal biomass increased by a factor of 2.6 when the cultivation broth was supplemented with 70 mg/L, which can be explained by the superior CO$_2$ biofixation mediated by the NPs [8]. Thus, the higher CO$_2$ availability mediated by CACOI NPs at 70 mg/L stimulated the activity of the RuBisCO enzyme, which is widely known to be the catalyst of CO$_2$ biofixation [13]. Therefore, an enhanced CO$_2$ biofixation resulted in an increased biomass productivity during the logarithmic growth phase, and in the accumulation of high-value products [13]. Hence, the improved logarithmic phase coupled to the accumulation of carbohydrates confirms that the biofixation capacity of microalgae was significantly improved by the addition of 70 mg/L of CACOI NPs.

Finally, the addition of 70 mg/L of SiO$_2$ NPs led to a cumulative CO$_2$ consumption 11.50% higher than that of the control, thus confirming that SiO$_2$ NPs acted as CO$_2$ adsorbents mediating a faster CO$_2$ dissolution in the algal broth. Notwithstanding, the addition of 40 and 70 mg/L of SiO$_2$ NPs resulted in a longer lag phase while no statistical
difference was observed on the Px. Even if the addition of SiO$_2$ NPs induced higher cumulative CO$_2$ consumptions, no statistical difference was observed neither in the cumulative O$_2$ production nor in OD$_{750}$, which did not agree with the observations of Jeon and co-workers [14]. The latter confirms the fact that the exposure to NPs is species specific and even if the addition of SiO$_2$ NPs has been reported to enhanced biomass and lipid production in *Chlorella vulgaris*, the mixed culture used in our study did not experience the same beneficial effects. Interestingly, the addition of SiO$_2$ NPs enhanced both the carbohydrate and lipid content of the final biomass regardless of the NPs concentration tested. For instance, the addition of 40 mg/L SiO$_2$ NPs supported the highest carbohydrate content, which was 1.91-fold higher than that in the control assays. Similarly, enhancements in the lipid content ranging by a factor 1.3-1.5 were obtained when SiO$_2$ NPs were supplemented to the algal broth. Thus, the superior accumulation of carbohydrates and lipids can be explained by the fact that the addition of SiO$_2$ NPs created a stress environment to the microalgae and, as a response, carbohydrates were accumulated as an energy reserve [43]. On the other hand, lipid accumulation can be explained by the fact that the SiO$_2$ NPs induced an oxidative stress to microalgae, resulting in a lipid accumulation as a non-enzymatic antioxidant mechanism of defense to scavenge the excessive ROS [44]. Similar findings have been reported by Jeon et al [14], who reported lipid enhancements of up to 340% compared to the control mainly attributed to the environmental stress created by the NPs. Thus, our results suggest that the SiO$_2$ NPs served as CO$_2$ adsorbents, however the nature of the NPs to created stress conditions that limited the growth of microalgae. Nonetheless, the SiO$_2$ NPs can be used as a technique to improve the value of the produced biomass.
3.4 Influence of nanoparticle concentration under UV-visible light

Solar UV radiation can seriously affect microalgal integrity and biological function, since it induces the production of ROS [45]. However, Yang et al. [12] recently proved that UV-light mediated a positive effect on CO$_2$ capture and lipid production in *C. pyrenoidosa* when graphene oxide quantum dots were added. In this context, NPs could act as UV protectors and/or spectrum converters to promote microalgal growth and macromolecule accumulation.

In our study, the addition of Fe$_2$O$_3$ NPs supported an enhancement of up to 50% in Px compared to the control (Table 5). However, no statistical difference was observed in the cumulative CO$_2$ consumption between the assays (Fig. 5). Furthermore, the cumulative O$_2$ decreased as the NPs concentration increased. Interestingly, despite the cumulative O$_2$ concentration was reduced by 30% at 70 mg/L Fe$_2$O$_3$ NPs, the OD$_{750}$ and Px were 26% and 5% higher than in the control, respectively. The latter suggests that when Fe$_2$O$_3$ NPs were added, the reduction in O$_2$ content in the headspace did not entail a lower cell growth and this particular behavior can be attributed to the interactions between O$_2$ and the NPs, which likely caused the formation of ROS. Additionally, the presence of 70 mg/L of Fe$_2$O$_3$ NPs resulted in a carbohydrate enhancement of up to 94% compared to the control assays. However, no statistical difference in term of lipid content was observed among the assays (Fig. 6). Moreover, the supply of UV light in this test series led to a higher lipid production compared to the assays conducted exclusively with visible light regardless of the addition of NPs. Thus, our results are in agreement with the observations of Yang et al. [12], who reported that the addition of graphene quantum dots enhanced the photosynthetic activity and the CO$_2$ fixation of *Chlorella pyrenoidosa* when exposed to UV-light. Additionally, Dinc et al [46] has also observed beneficial effects on *C. vulgaris* growth by the addition of
Se NPs under UV light, mainly because the NPs scavenge the UV radiation, protecting the microalgal cells. Thus, the Fe$_2$O$_3$ NPs herein used stimulated microalgae growth at the highest concentration tested, suggesting that Fe$_2$O$_3$ can scavenge the harmful effect of UV radiation resulting in high-value biomass productivity.
**Fig. 5.** Time course of the cumulative CO$_2$ consumption in the assays supplied with different concentrations of a) Fe$_2$O$_3$ NPs, b) CACOI NPs, c) SiO$_2$ NPs; of the cumulative O$_2$ production in the tests supplemented with different concentrations of d) Fe$_2$O$_3$ NPs, e) CACOI NPs, f) SiO$_2$ NPs; and culture absorbance of the algal consortium supplied with different concentrations of g) Fe$_2$O$_3$ NPs, h) CACOI NPs, i) SiO$_2$ NPs. The assays were run under UV+visible light. CACOI: carbon coated zero valent iron; NPs: nanoparticles.

On the other hand, despite the increase in CACOI NPs concentration from 20 to 70 mg/L did not enhance Px, the addition of 70 mg/L of NPs resulted in a faster exponential phase and a statistically significant CO$_2$ consumption enhancement. Interestingly, there was no statistical difference in the cumulative O$_2$ production between the assays, and the lipid production slightly decreased as the NPs concentration increased. Since this behavior was not observed in the assays carried out only with visible light, the latter suggest that lipid
peroxidation in this particular test series was induced by ROS formation mediated by the interaction of the zero valent iron contained in the NPs and the UV light exposure [12]. However, the addition of 70 mg/L induced a carbohydrate content enhancement of up to 22% and an OD\textsubscript{750} 15% higher than the control. The results herein obtained confirm the fact that CACOI NPs effect of microalgae are mainly as CO\textsubscript{2} adsorbents, resulting in enhanced CO\textsubscript{2} availability in the headspace of the bottles. Moreover, the increased CO\textsubscript{2} led to an activation of microalgae metabolism and storage as carbohydrates under both visible and visible + UV light.

Finally, the addition of SiO\textsubscript{2} NPs did not support an enhancement in Px despite the addition of 70 mg/L SiO\textsubscript{2} NPs led to a CO\textsubscript{2} consumption 18% higher than that recorded in the control tests. Moreover, the addition of 20 and 40 mg/L of SiO\textsubscript{2} NPs led to 11% and 6% higher O\textsubscript{2} cumulative productions compared to the control tests, respectively. Additionally, OD\textsubscript{750} increased as the NPs concentration increased, and the addition of 70 mg/L SiO\textsubscript{2} induced a OD\textsubscript{750} enhancement of 16%. Furthermore, the addition of 70 mg/L SiO\textsubscript{2} mediated a 69% enhancement in the lipid content compared to the control. Finally, our results indicate that the UV-light exposure induce a higher lipid accumulation in microalgae likely due to a mechanism of defense against the generation of ROS [47]. Interestingly, SiO\textsubscript{2} NPs and UV radiation can induce an oxidative stress on microalgae [14]. However, in our particular study, neither biomass loss nor lipid peroxidation by the combination of SiO\textsubscript{2} NPs and UV radiation was observed. Therefore, our results suggest that the oxidative stress caused by SiO\textsubscript{2} NPs did not increase with UV exposure. Thus, even if no biomass enhancements were observed with the addition of SiO\textsubscript{2} NPs neither under visible and visible + UV light exposure, contrary to the observed by Jeon et al [14], these NPs still can be used as a strategy to produce high-value biomass even under UV radiation.
4. Conclusions and future prospectives

Fe$_2$O$_3$, CACOI and SiO$_2$ NPs addition to microalgal cultures devoted to biogas upgrading boosted CO$_2$ adsorption resulting in high-value biomass. Under visible light, the cumulative CO$_2$ consumptions increased as the NPs concentrations increased. SiO$_2$ NPs stimulated carbohydrates and lipids production, CACOI NPs supported both increased CO$_2$ consumptions, higher biomass productivities, shorter lag phases and carbohydrate productions. UV light supply reduced the beneficial effects of NPs, however, the addition of Fe$_2$O$_3$ NPs stimulated biomass productivities and carbohydrates, whereas CACOI NPs supported shorter lag phases, increased CO$_2$ consumption and carbohydrates productions. Finally, the addition of SiO$_2$ NPs supported lipid production enhancements. Promising results to improve the CO$_2$ adsorption couple to biomass production and high-value products were obtained in the present study. However, it is important to highlight that these particular results were obtained under controlled conditions. In this regard, future studies should be directed to assessed the effect of the NPs on microalgae under uncontrolled conditions, i.e. real centrate and environmental conditions. Moreover, life cycle assessments, exergy analyses, techno-economic analyses and energy analyses as described in [48], should be considered to assess the sustainability of the process. Finally, the results herein obtained can be scaled-up to pilot plants to boost CO$_2$ consumption coupled to microalgae growth. The later could represent a feasible technique to improve the performance of the established technology for photosynthetic biogas upgrading.

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CRediT authorship statement

Laura Vargas-Estrada: methodology, writing-original draft; Edwin G. Hoyos: methodology, P.J. Sebastian: reviewing, Raúl Muñoz: supervision, reviewing and editing.
Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
Graphical abstract

Elucidating the role of nanoparticles on photosynthetic biogas upgrading

Biogas A
70% CH₄
30% CO₂

Fe₂O₃
CACOI
SiO₂
Enhanced CO₂ consumption

Biogas B
70% CH₄
29.5% CO₂
0.5% H₂S

Fe₂O₃
CACOI
SiO₂
Microalgae inhibition

Visible light

Biogas A
70% CH₄
30% CO₂

Fe₂O₃
CACOI
SiO₂
20, 40, 70 mg/L
Enhanced:
CO₂ consumption
Microalgae metabolism
Carbohydrates/lipids production

Visible + UV light

Biogas A
70% CH₄
30% CO₂

Fe₂O₃
CACOI
SiO₂
20, 40, 70 mg/L
Reduced beneficial effects of nanoparticles
Highlights

- Metal nanoparticles acted as CO$_2$ adsorbents during photosynthetic biogas upgrading
- Carbon coated iron nanoparticles increased the carbohydrate content up to 260%
- The addition of 70 mg/L SiO$_2$ nanoparticles enhanced by 69% the lipid content
- UV light supplementation to visible light reduced the beneficial effects of nanoparticles