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# Seasonal variation of biogas upgrading coupled with digestate treatment in an outdoors pilot scale algal-bacterial photobioreactor

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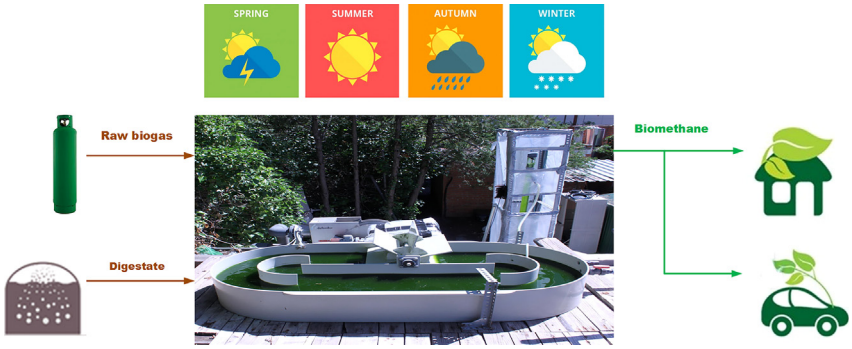
## GRAPHICAL ABSTRACT

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## ABSTRACT

The yearly variations of the quality of the upgraded biogas and the efficiency of digestate treatment were evaluated in an outdoors pilot scale high rate algal pond (HRAP) interconnected to an external absorption column (AC) via a conical settler. $CO_2$ concentrations in the upgraded biogas ranged from 0.7% in August to 11.9% in December, while a complete $H_2S$ removal was achieved regardless of the operational month. $CH_4$ concentrations ranged from 85.2% in December to 97.9% in June, with a limited $O_2$ and $N_2$ stripping in the upgraded biogas mediated by the low recycling liquid/biogas ratio in the AC. Biomass productivity ranged from 0.0 $g\,m^{-2}\,d^{-1}$ in winter to 22.5 $g\,m^{-2}\,d^{-1}$ in summer. Finally, microalgae diversity was severely reduced throughout the year likely due to the increasing salinity in the cultivation broth of the HRAP induced by process operation in the absence of effluent.

## 1. Introduction

Biogas from the anaerobic digestion (AD) of organic waste and wastewater constitutes a renewable energy vector able to reduce the consumption of fossil fuels. Biogas is typically composed of $CH_4$ (40–75%), $CO_2$ (15–60%) and minor components such as $H_2S$ (0.005–2%), $N_2$ (0–2%), $O_2$ (0–1%), $NH_3$ (< 1%), CO (< 0.6%), siloxanes (0–0.2%) and halogenated hydrocarbons (VOC < 0.6%) (Ryckebosch et al., 2011). The increasing relevance of biogas in the EU-28 energy sector has increased by a factor of 3 the number of plants

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from 6227 in 2009 to 17,662 by the end of 2016 (European Biogas Association, 2016). This green energy vector can be used to produce either electricity and heat in industry or domestic heat, as a feedstock in fuel cells or as substitute of natural gas (Andriani et al., 2014; Muñoz et al., 2015). In this regard, the upgrading of biogas prior injection into natural gas grids or use as a vehicle fuel is mandatory according to most international regulations, which require a biomethane composition of: $CH_4 \geq 95\%$, $CO_2 \leq 2–4\%$, $O_2 \leq 1\%$ and negligible amounts of $H_2S$ (Muñoz et al., 2015). The removal of the major biogas contaminant, $CO_2$, decreases the transportation costs of biomethane and increases its specific calorific value, while the removal of $H_2S$ effectively limits the corrosion in pipelines, engines and biogas storage structures (Posadas et al., 2015).

Multiple physical-chemical technologies are nowadays commercially available to remove $CO_2$ and $H_2S$ from biogas. Pressure swing adsorption, membrane separation, cryogenic separation or chemical/water/organic scrubbing provide the required levels of $CO_2$ removal for biomethane injection. On the other hand, adsorption on activated carbon or metal ions, *in situ* chemical precipitation, membrane separation and absorption in conventional gas-liquid contactors are typically applied to desulphurise biogas (Toledo-cervantes et al., 2017). Nevertheless, these commercial processes must be implemented sequentially to abate $H_2S$ prior $CO_2$ separation, which increases both CAPEX and OPEX (Muñoz et al., 2015; Toledo-cervantes et al., 2017b). Likewise, several biological technologies are nowadays available to remove $CO_2$ and $H_2S$ from biogas, although most of them have been only validated at pilot scale. Thus, chemoautotrophic biogas upgrading (using a power to gas strategy) can provide the required levels of $CO_2$ removal, while *in situ* micro-aerobic AD or biofiltration are typically applied to remove $H_2S$ from biogas (Farooq et al., 2018; Muñoz et al., 2015). Similarly to their physical-chemical counterparts, these biological processes can only support the individual removal of $CO_2$ or $H_2S$, which also entails the need for a two-stage upgrading (with the subsequent increase in investment and operational costs). In this context, algal-bacterial processes have recently emerged as a cost-effective and environmentally friendly alternative to conventional biogas upgrading techniques due to their ability to simultaneous remove $CO_2$ and $H_2S$ in a single stage process (Bahr et al., 2014).

Biogas upgrading in algal-bacterial photobioreactors is based on the photosynthetic fixation of $CO_2$ by microalgae and the concomitant oxidation of $H_2S$ to $SO_4^{2-}$ by sulfur oxidizing bacteria mediated by the high dissolved oxygen (DO) concentrations present in the cultivation broth as a result of photosynthetic activity (Toledo-Cervantes et al., 2016). The environmental sustainability and cost-competitiveness of this technology can be improved via digestate supplementation as the nutrient source to support microbial growth (Toledo-Cervantes et al., 2016). In this regard, the optimization of photosynthetic biogas upgrading coupled to digestate treatment has been recently carried out indoors under artificial illumination in high rate algal ponds (HRAPs) interconnected to biogas absorption columns (AC). Bahr et al. (2014) were the first to evaluate the potential of microalgal-bacterial consortium for the simultaneous removal of $H_2S$ and $CO_2$ from biogas. Meier et al. (2015) focused their work on the development of a process for photosynthetic biogas upgrading using *Nannochloropsis gaditana* as model microalgae in a batch test. Serejo et al. (2015) evaluated the influence of biogas flow rate and the liquid/biogas ratio in the composition of the upgraded biogas, while Posadas et al. (2016) optimized the biogas upgrading process in a HRAP using centrate with multiple nutrient composition. This process optimization provided promising results in terms of wastewater treatment (total nitrogen (TN)-removal efficiencies (REs) of 98.0 ± 1.0% and $P\text{-}PO_4^{3-}$ REs of 100 ± 0.5%) and biomethane quality ($CH_4$ concentration of 96.2 ± 0.7%) (Toledo-cervantes et al., 2017). Likewise, comparable results were achieved by Posadas et al. (2017a,b) in a similar photobioreactor configuration operated outdoors during summer, when both solar irradiation, the number of sun hours and temperatures were furthermost favorable to algal-bacterial activity. Therefore, a systematic evaluation for the influence of a year-round variations of environmental conditions on biogas purification and nutrient recovery from digestate is needed to validate this technology under outdoor conditions.

This study investigated for the first time the simultaneous upgrading of biogas and treatment of digestate in an pilot HRAP interconnected to an external AC via a conical settler over one year of outdoors operation to determine the influence of environmental conditions on process performance. The process was operated using a novel strategy to decouple biomass productivity from the hydraulic retention time via control of the biomass wastage rate from the settler in order to maximize the recovery of carbon and nutrients in the form of algal-bacterial biomass. Finally, the dynamics of microalgae population structure were also investigated.

## 2. Materials and methods

### 2.1. Biogas and digestate

The synthetic gas mixture used as a model biogas was composed of $CO_2$ (29.5%), $H_2S$ (0.5%) and $CH_4$ (70%) (Abello Linde; Spain). The digestate here used was monthly obtained from the centrifuges dehydrating the anaerobically digested sludge of the wastewater treatment plant (WWTP) of Valladolid and stored at 4 °C. Digestate composition was subjected to variations along the experimental period due to the seasonal operational variations of the WWTP: total organic carbon (TOC) concentrations of 16–523 mg $L^{-1}$, inorganic carbon (IC) concentrations of 450–600 mg $L^{-1}$, TN concentrations of 374–718 mg $L^{-1}$, $P\text{-}PO_4^{3-}$ concentrations of 26–135 mg $L^{-1}$ and $SO_4^{2-}$ concentrations of 0–38 mg $L^{-1}$. IC concentration was increased to 1999 ± 26 mg $L^{-1}$ via addition of $NaHCO_3$ and $Na_2CO_3$ to maintain the high buffer capacity and pHs (≥9) required in the cultivation broth to support an effective biogas upgrading (Posadas et al., 2017a,b).

### 2.2. Experimental set-up

The photobioreactor set-up was built outdoors at Valladolid University (41.39° N, 4.44° W) according to Posadas et al. (2017a,b). The pilot experimental plant consisted of a 180 L HRAP with an illuminated area of 1.20 $m^2$ (width = 82 cm; length = 170 cm; depth = 15 cm) and two water channels divided by a central wall and baffles in each side of the curvature. The cultivation broth in the HRAP was continuously agitated by a 6-blade paddlewheel at an internal liquid velocity of ≈20 cm $s^{-1}$. The HRAP was interconnected to a separate 2.5 L bubble absorption column (internal diameter = 4.4 cm; height = 165 cm) provided with a metallic biogas diffuser of 2 μm pore size situated at the bottom of the column. The HRAP and the AC were interconnected via an external liquid recirculation of the supernatant of the algal-bacterial cultivation broth from an 8 L settler (Fig. 1; Table A.1).

### 2.3. Operational conditions and sampling procedures

Process operation was carried out from November the 1st 2016 to October the 30st 2017. The HRAP was inoculated at an initial concentration of 210 mg total suspended solids (TSS) $L^{-1}$ with a microalgal inoculum composed of (percentage expressed in number of cells) *Leptolyngbya lagerheimii (54%), Chlorella vulgaris (28%), Parachlorella kessleri (9%), Tetradesmus obliquus (5%) and Mychonastes homosphaera (2%)* from a previous culture grown in an indoor HRAP located at the Department of Chemical Engineering and Environmental Technology of Valladolid University (Spain). Five operational stages (namely I, II, III, IV and V) were defined as a function of the environmental conditions, which ultimately determined the biomass productivity set in our experimental system (Table 1). The HRAP was fed with digestate as a nutrient source at a flow rate of 3.5 L $d^{-1}$. The synthetic biogas was