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Influence of alkalinity and temperature on photosynthetic biogas upgrading efficiency in high rate algal ponds

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ABSTRACT

Algal-bacterial photobioreactors have emerged as a cost-effective platform for biogas upgrading. The influence on biomethane quality of the inorganic carbon concentration (1500, 500 and 100 mg L^{-1}) and temperature (12 and 35 °C) of the cultivation broth was evaluated in a 180 L high rate algal pond (HRAP) interconnected to a 2.5 L absorption column via settled broth recirculation. The highest CO_2 and H_2S removal efficiencies (REs) from biogas were recorded at the highest alkalinity (CO_2-REs of 99.3 ± 0.1 and 97.8 ± 0.8% and H_2S-REs of 96.4 ± 2.9 and 100 ± 0% at 12 and 35 °C, respectively), which resulted in CH_4 concentrations of 98.9 ± 0.2 and 98.2 ± 1.0% at 12 and 35 °C, respectively, in the upgraded biogas. At the lowest alkalinity, the best upgrading performance was observed at 12 °C (CO_2 and H_2S-REs of 41.5 ± 2.0 and 80.3 ± 3.9%, respectively). The low recycling liquid to biogas ratio applied (0.5) resulted in a negligible O_2 stripping regardless of the alkalinity and temperature, which entailed a biomethane O_2 content ranging from 0 to 0.2 ± 0.3%.

1. Introduction

Biogas from the anaerobic digestion of organic matter constitutes a promising renewable energy vector for the production of heat and power in households and industry [1]. Raw biogas is mainly composed of CH_4 (40–75%), CO_2 (25–50%) and other components at lower concentrations such as H_2S (0.005–2%), oxygen (0–1%), nitrogen (0–2%), siloxanes (0–0.02%), ammonia (< 1%) and halogenated hydrocarbons (VOC < 0.6%) [2]. The high content of CO_2 significantly reduces the specific calorific value of biogas, increases its transportation costs and promotes emissions of CO and hydrocarbons during combustion. On the other hand, H_2S is a toxic and malodorous gas that severely reduces the lifespan of the biogas storage structures, pipelines, boilers and internal combustion engines [3]. The removal of these biogas pollutants is mandatory in order to comply with the technical specifications required for biogas injection into natural gas grids (CH_4 > 95%, CO_2 < 2.5–4%, O_2 < 0.001–1% and H_2S + COS < 5 mg/Nm^3) or use as a vehicle fuel [4]. State-of-the-art physical/chemical or biological technologies for CO_2 removal often need a previous H_2S cleaning step, while the few technologies capable of simultaneously removing CO_2 and H_2S from biogas (i.e. water/chemical scrubbing and membrane separation) exhibit a high energy and chemicals consumption, which limits their economic and environmental sustainability for biogas upgrading [5]. In this context, algal-bacterial symbiosis represents a cost-effective and environmentally friendly platform for the simultaneous removal of CO_2 and H_2S from raw biogas in a single step process [6].

Photosynthetic biogas upgrading in algal-bacterial photobioreactors is based on the light-driven CO_2 consumption by microalgae coupled to the oxidation of H_2S to either elemental sulfur or sulfate by sulfur-oxidizing bacteria (i.e. belonging to the Thioalbus genus) using the oxygen photosynthetically produced [3, 7]. The environmental and economic sustainability of the process can be boosted with the integration of wastewater treatment in the photobioreactor devoted to biogas upgrading [8]. In this regard, digestate or domestic wastewater can be used as an inexpensive nutrient source for microalgae and bacteria growth during photosynthetic biogas upgrading, which in turn would reduce the costs associated to nutrients removal [9, 10]. Recent investigations have focused on the optimization of the simultaneous biogas upgrading and digestate treatment in photobioreactors. These studies have identified the optimum photobioreactor configuration [6, 8, 11, 12], the strategies for minimizing oxygen concentration in the biomethane [13, 14] and the influence of light intensity, wavelength and photoperiod regime on the final quality of the upgraded biogas under indoors conditions [15–19]. Unfortunately, most of these previous works did not result in a biomethane composition complying with

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the specifications of most European regulations due to the limited CO_2 mass transfer rates from the raw biogas to the aqueous phase [20]. In this context, a recent study conducted outdoors in a high rate algal pond (HRAP) interconnected to an external absorption column for the simultaneous treatment of biogas and centrate suggested that both alkalinity and temperature in the algal-bacterial broth can play a key role on the final biomethane quality [11]. Indeed, culture broth alkalinity determines the kinetics of both microalgae growth in the HRAP and CO_2/H_2S absorption in the absorption column [21]. Likewise, culture broth temperature directly impacts on the gas/liquid equilibria and biomass growth kinetics [19]. However, despite the relevance of these environmental parameters on the performance of photosynthetic biogas upgrading, no study has evaluated to date the effect of alkalinity and temperature on the final quality of biomethane in algal-bacterial photobioreactors.

This work systematically evaluated the influence of inorganic carbon concentration and temperature in the cultivation broth on biomethane quality in a 180 L HRAP interconnected to a 2.5 L absorption column via external recirculation of the settled cultivation broth under indoor conditions. The tested inorganic carbon concentrations (1500, 500 and 100 mg L^{-1}) are typically encountered in high and medium strength digestates and domestic wastewater, respectively, while the tested temperatures are representative of spring-autumn (12 °C) and summer (35 °C) seasons in temperate climates.

2. Materials and methods

2.1. Biogas and centrate

A synthetic gas mixture composed of CO_2 (29.5%), H_2S (0.5%) and CH_4 (70%), was used in this study as a model biogas (Abello Linde; Spain). Centrate was collected from the anaerobically digested sludge-dehydrating centrifuges at Valladolid wastewater treatment plant (WWTP) and stored at 4 °C prior to use. The average centrate composition was as follows: inorganic carbon (IC) = 459 ± 83 mg L^{-1}, total nitrogen (TN) = 576 ± 77 mg L^{-1} and S-SO_4^{2-} = 4.7 ± 3.4 mg L^{-1}. NH_4Cl was added to the raw centrate to a final TN concentration of 1719 ± 235 mg L^{-1} in order to simulate a high-strength digestate and thus minimize the flow rate of centrate used in the pilot plant.

2.2. Experimental set-up

The experimental set-up was located at the Department of Chemical Engineering and Environmental Technology at Valladolid University (Spain). The set-up consisted of a 180 L HRAP (depth: 15 cm, width: 63 cm, length: 202 cm) with an illuminated surface of 1.2 m^2 divided by a central wall in two water channels. The HRAP was interconnected to a 2.5 L absorption column (Ø: 4.4 cm, height: 165 cm) via external liquid recirculation of the supernatant of the algal-bacterial cultivation broth from a 10 L conical settler coupled to the HRAP (Fig. 1). The remaining algal bacterial biomass collected at the bottom of the settler was continuously recirculated to the HRAP in order to avoid the development of anaerobic conditions in the settler due to an excessive biomass accumulation. The HRAP cultivation broth was continuously agitated by a 6-blade paddlewheel at an internal recirculation velocity of ≈20 cm s^{-1}. A photosynthetic active radiation (PAR) of 1350 ± 660 μmol m^{-2} s^{-1} at the HRAP surface was provided by six high-intensity LED PCBs (Phillips SA, Spain) operated in a 12 h:12 h light/dark regime.

2.3. Operational conditions

Six operational conditions were tested in order to assess the influence of alkalinity and temperature on biomethane quality. The influence of IC concentrations of 1500, 500 and 100 mg L^{-1} was evaluated in stages I–II, III–IV and V–VI, respectively, while a temperature of 35 °C was maintained during stages I, III and V and a temperature of 12 °C during stages II, IV and VI (Table 1). The HRAP was initially filled with an aqueous solution containing a mixture of $NaHCO_3$ and Na_2CO_3 before inoculation to adjust the initial IC concentration to the corresponding concentration set in the operational stage. The IC concentration of the digestate fed to the HRAP during each operational stage was also adjusted accordingly. Thus, IC concentrations of 1500 and 500 mg L^{-1} were obtained by addition of $NaHCO_3$ to the raw centrate, while IC concentrations of 100 mg L^{-1} were achieved via an initial centrate acidification with HCl aqueous solution (37%) to a final pH of 5.5 in order to remove IC by air-aided CO_2 stripping followed by $NaHCO_3$ addition to adjust the IC concentration. The temperature of the HRAP cultivation broth was controlled with an external heat exchanger (Fisherbrand™ Polystat™ Immersion Circulator, Germany). A consortium of microalgae/cyanobacteria (from now on referred to as microalgae) from outdoors HRAPs treating centrate and domestic wastewater at the Department of Chemical Engineering and Environmental Technology at Valladolid University and at the WWTP of Chiclana de la Frontera (Spain), respectively, was used as inoculum in each operational stage.

During the illuminated periods, the HRAP was fed with the modified digestate as a nutrient source at a flow rate of 2 L d^{-1} while synthetic biogas was sparged into the absorption column under co-current flow operation at a flow rate of 4.9 L h^{-1} and a recycling liquid flow rate (L min^{-1}) to biogas flow rate (L min^{-1}) ratio (L/G, dimensionless) of 0.5 [12]. Tap water was continuously supplied in order to compensate water evaporation losses. A biomass productivity of 7.5 g dry matter m^{-2} d^{-1} was set in the six operational stages evaluated by controlling the biomass harvesting rate. The algal-bacterial biomass was harvested by sedimentation after coagulation-flocculation via addition of the polyacrylamide-based flocculant Chemifloc CV-300 (Chemipol S.A) [22]. This operational strategy resulted in a process operation without effluent. Approximately two weeks after the beginning of each stage, the system had already achieved a steady state, which was confirmed by the negligible variation of most parameters during the rest of the stage (variations < 5% of the recorded values).

2.4. Sampling procedure

The ambient and cultivation broth temperatures, the flow rates of digestate, tap water and external liquid recycling, and the dissolved oxygen (DO) concentration in the cultivation broth were monitored three times per week during the illuminated and dark periods. The PAR was measured at the HRAP surface at the beginning of each stage. Gas samples of 100 μL from the raw and upgraded biogas were drawn three times per week in order to monitor the CO_2, H_2S, CH_4, O_2 and N_2 concentrations. The inlet and outlet biogas flow rates at the absorption column were also measured to accurately determine CO_2 and H_2S removals. Liquid samples of 100 mL of digestate and cultivation broth were drawn three times per week and filtered through 0.20 μm nylon filters to monitor pH, dissolved IC, TN and SO_4^{2-}. In addition, liquid samples of 20 mL were also drawn three times per week from the cultivation broth to monitor the TSS concentration. Unfortunately, no analysis of the microbial population structure was conducted in this study.

2.5. Analytical methods

The DO concentration and temperature were monitored with an OXI 330i oximeter (WTW, Germany), while a pH meter Eutech Cyberscan pH 510 (Eutech instruments, The Netherlands) was used for pH determination. The PAR at the HRAP surface was recorded with a LI-250A lightmeter (LI-COR Biosciences, Germany). CO_2, H_2S, O_2, N_2 and CH_4 gas concentrations were analysed using a Varian CP-3800 GC-TCD (Palo Alto, USA) according to Posadas et al. [13]. The dissolved IC and TN concentrations were determined using a Shimadzu TOC-VCSH

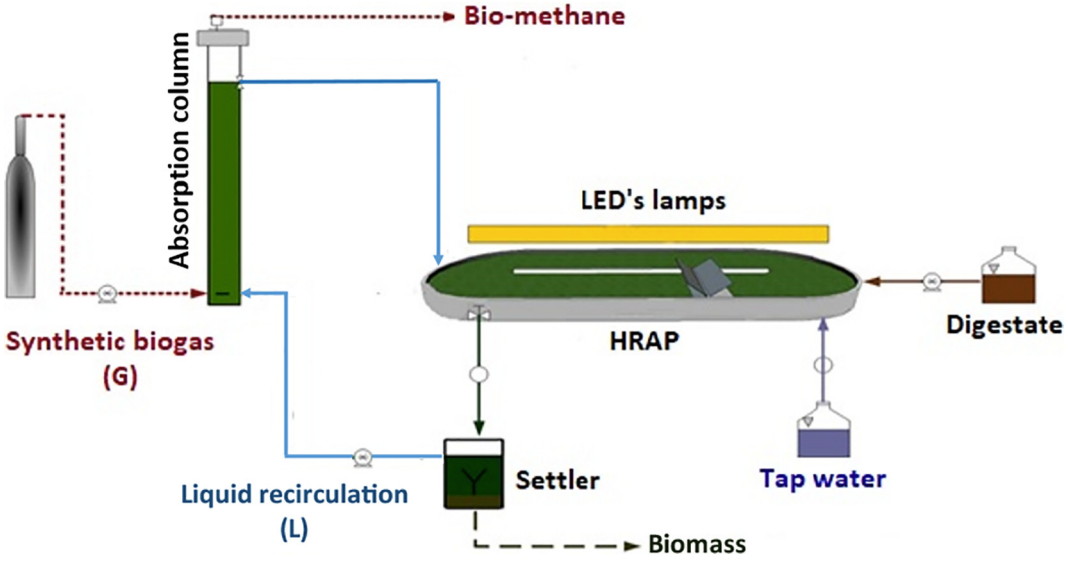

Fig. 1. Schematic diagram of the experimental set-up.

Table 1
Average environmental parameters along with the corresponding standard deviation (n = 4) in the HRAP, absorption column and digestate under steady state conditions during the six operational stages tested.

Stage	I	II	III	IV	V	VI
Average IC feed ($mg\,L^{-1}$)	1581 ± 135	1467 ± 115	505 ± 57	517 ± 46	102 ± 7	103 ± 11
Average Temperature (°C)	35.0 ± 1.3	12.5 ± 1.8	36.0 ± 1.2	12.4 ± 2.0	36.0 ± 1.6	12.9 ± 1.8
Evaporation rate ($L\,m^{-2}\,d^{-1}$)	14.1 ± 0.2	2.3 ± 0.4	15.8 ± 1.1	1.6 ± 0.3	17.5 ± 0.1	1.8 ± 0.3
DO light ($mg\,L^{-1}$)	10.1 ± 2.1	14.4 ± 0.9	13.5 ± 0.8	16.6 ± 1.9	8.8 ± 0.8	16.5 ± 1.7
DO dark ($mg\,L^{-1}$)	1.3 ± 0.0	6.2 ± 1.2	3.7 ± 0.1	7.0 ± 0.9	4.6 ± 0.6	10.0 ± 0.5
pH HRAP	11.0 ± 0.0	10.5 ± 0.3	10.5 ± 0.4	9.7 ± 0.2	7.2 ± 0.3	7.5 ± 0.2
pH outlet column	10.4 ± 0.1	9.9 ± 0.2	7.3 ± 0.1	6.9 ± 0.1	5.3 ± 0.2	5.5 ± 0.1
Average IC HRAP ($mg\,L^{-1}$)	1667 ± 157	1891 ± 31	321 ± 52	367 ± 23	4 ± 1	7 ± 2
TSS ($g\,L^{-1}$)	0.43 ± 0.02	0.54 ± 0.05	0.44 ± 0.07	0.45 ± 0.02	0.20 ± 0.07	0.18 ± 0.03
S-SO_4^{2-} accumulation ($g\,m^{-3}\,d^{-1}$)	1.85	1.10	1.57	0.97	1.33	0.60
Duration (d)	26	28	29	27	28	26

IC: inorganic carbon; DO: dissolved oxygen; TSS: total suspended solids.

analyser (Japan) equipped with a TNM-1 chemiluminescence module. SO_4^{-2} concentration was measured by HPLC-IC according to Posadas et al. [23], while the determination of TSS concentration was carried out according to standard methods [24].

2.6. Statistical treatment

The ambient and cultivation broth temperatures, pH, cultivation broth TSS concentrations, the flow rates of digestate, tap water and external liquid recycling, the dissolved oxygen (DO) concentration, and the flowrate and composition of biogas were obtained under steady state operation. CO_2-REs and H_2S-REs were calculated according to [13] based on duplicate measurements of the biogas and biomethane composition. The results here presented were provided as the average values (obtained for at least 4 sampling days over a two week period during each steady state) along with their corresponding standard deviation.

A t-student statistical analysis was performed in order to determine the statistically significant differences between the pH value at the bottom and the top of the absorption column. In addition, the t-student test was applied to determine the effect of temperature at the different alkalinities tested. Finally, a one-way ANOVA was performed to determine the effect of alkalinity and temperature on the quality of the biomethane produced along the six operational stages.

3. Results and discussion

3.1. Environmental parameters and biomass concentration

The average water loss by evaporation in the HRAP (average tap water flow rate needed to maintain the level of the HRAP constant) during process operation at 35 °C was 15.9 ± 1.2 $L\,d^{-1}\,m^{-2}$, while this value decreased to 1.9 ± 0.4 $L\,d^{-1}\,m^{-2}$ at 12 °C (Table 1). The maximum evaporation rate recorded in this study was ~1.8 times higher than the maximum reported by Posadas et al. [11] in a similar outdoors HRAP during summer in a temperate climate and ~2.6 times higher than the highest value estimated by Guieysse et al. [25] in an arid location. The high water losses here recorded were caused by the high and constant temperatures of the cultivation broth throughout the entire day (no decrease in the culture broth temperature occurred during the night) and the high turbulence induced by the oversized paddlewheel typical in lab-scale systems [25]. On the other hand, the lower temperature prevented water losses, the minimum value recorded being in the range obtained by Posadas et al. [26] in a similar outdoors HRAP during spring in a temperate climate (3 ± 8 $L\,m^{-2}\,d^{-1}$).

The average DO concentrations in the cultivation broth during the illuminated period (~6 h after turning on the lights) were 10.1 ± 2.1, 14.4 ± 0.9, 13.5 ± 0.8, 16.6 ± 1.9, 8.8 ± 0.8 and 16.5 ± 1.7 mg $O_2\,L^{-1}$ during stages I, II, III, IV, V and VI, respectively; while the DO concentrations during the dark period (~6 h after turning off the lights) averaged 1.3 ± 0.5, 6.2 ± 1.2, 3.7 ± 0.1, 7.0 ± 0.9,

4.6 ± 0.6 and 10.0 ± 0.5 mg O_2 L^{-1} in stages I to VI, respectively. The higher DO concentrations recorded at 12 °C were attributed to the increased oxygen solubility at low temperatures [27]. No pernicious effect of these DO concentrations on microalgae activity was expected since inhibition of photosynthesis typically occurs above 25 mg O_2 L^{-1}, and the values remained within the optimal range to support nutrients and CO_2 bioassimilation [28].

The average pHs in the HRAP during stages I, II, III, IV, V and VI were 11.0 ± 0.0, 10.5 ± 0.3, 10.5 ± 0.4, 9.7 ± 0.2, 7.2 ± 0.3 and 7.5 ± 0.2, respectively. These findings confirmed that the influence of the IC concentration in the cultivation broth was higher than that of the temperature on the steady state pH of the cultivation broth, which was in accordance with previous results from Posadas et al. [11]. Moreover, the highest pH values here recorded matched those observed by Toledo-Cervantes et al. [12] during the simultaneous treatment of biogas and digestate in a similar experimental set-up, while Lebrero et al. [20] reported comparable pHs to the lowest values obtained in this study when evaluating biogas upgrading in a transparent PVC column photobioreactor. A higher pH in the cultivation broth enhances the mass transfer rate of the acidic gases (CO_2 and H_2S) from biogas to the liquid phase, which ultimately results in higher upgrading performances as discussed below [6].

TSS concentrations of 0.4–0.5 g L^{-1} were recorded during process operation at both high and medium alkalinity (Table 1). Thus, the biomass concentration in the cultivation broth at the imposed biomass productivity (7.5 g dry matter m^{-2} d^{-1}) during stages I to IV was representative of the operation of conventional outdoor raceways, where TSS concentration typically ranges from 0.3 to 0.5 g L^{-1} [29]. However, the biomass concentration and productivity, during stages V and VI (IC concentration of 100 mg L^{-1}), decreased to 0.2 g TSS L^{-1} and 5–7 g dry matter m^{-2} d^{-1} respectively, due to the lower carbon load supplied in the feed and the lower CO_2 mass transfer in the absorption column mediated by the low pH of the cultivation broth (as discussed in Section 3.2.1).

3.2. Biogas upgrading efficiency

3.2.1. CO_2-removal efficiency

Average CO_2-REs of 99.3 ± 0.1, 97.8 ± 0.8, 48.3 ± 3.6, 50.6 ± 3.0, 30.8 ± 3.6 and 41.5 ± 2.0% were recorded during stages I, II, III, IV, V and VI, respectively (Fig. 2).

During stages I and II (1500 mg IC L^{-1}), the high CO_2 mass transfer rates between the biogas and the liquid phase were promoted by the high pH (> 10.5) and high buffer capacity of the cultivation broth. The initial pH of the system (pH = 10.5) was roughly maintained in the cultivation broth of the HRAP (10.4 ± 0.1) and along the absorption column (9.9 ± 0.2) as a result of the high alkalinity of the digestate (Table 1). During stages III and IV (500 mg IC L^{-1}), a slight decrease in the pH of the cultivation broth from the initial value occurred as a result of biogas absorption in the column due to both the acidic nature of CO_2 and H_2S and the lower buffer capacity of the media, thus resulting in lower CO_2-REs. This effect was more pronounced in stages V and VI (100 mg IC L^{-1}), where the low buffer capacity of the cultivation broth was unable to maintain a constant and high pH, which resulted in the lowest CO_2-REs recorded in this experiment (Table 1). The pH of the cultivation broth significantly differed (t-student test, $p < 0.05$) between the bottom (10.5 ± 0.4, 9.7 ± 0.2, 7.2 ± 0.3 and 7.5 ± 0.2 in stages III, IV, V and VI, respectively) and the top (7.3 ± 0.1, 6.9 ± 0.1, 5.3 ± 0.2 and 5.5 ± 0.1 in stages III, IV, V and VI, respectively) of the absorption column at medium and low alkalinity (Table 1). Higher L/G ratios would have avoided these high pH variations along the absorption column. Nevertheless, a lower biomethane quality would be expected at high L/G ratios as a result of the enhanced O_2 and N_2 stripping from the recycling cultivation broth to the upgraded biogas [8]. These data was in accordance to Lebrero et al. [20], who reported an average CO_2-RE of 23% at a pH 7 and of 62% when the pH of the cultivation broth was increased up to 8.1. Overall, these results showed the relevance of inorganic carbon concentration to maintain a high pH in the scrubbing cultivation broth during biogas upgrading.

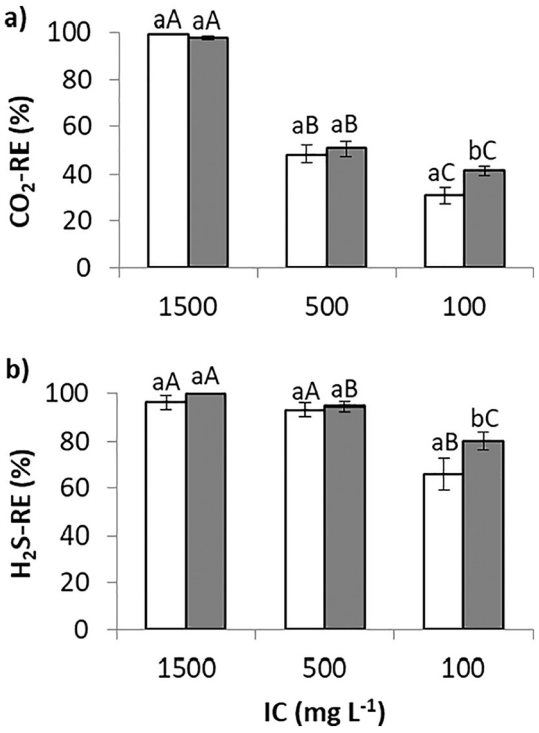

Fig. 2. Influence of the inorganic carbon concentration (IC) and temperature on the removal efficiency (RE) of a) carbon dioxide (CO_2) and b) hydrogen sulphide (H_2S) at 35 °C (□) and at 12 °C (■), average removal efficiencies and their standard deviation (n = 8). Similar lowercase letters indicate no significant differences ($p > 0.05$) when comparing both temperatures at each IC concentration. Similar uppercase letters indicate no significant differences ($p > 0.05$) when comparing the IC concentrations at the same temperature.

On the other hand, a negligible effect of the temperature on CO_2-RE was found at high and medium alkalinity (from stages I to IV) (Fig. 2). However, the higher CO_2 solubility at lower temperatures resulted in a higher CO_2-RE at 12 °C compared to that achieved at 35 °C under low alkalinity (stages V and VI) (Fig. 2). This suggests that, despite the lower alkalinity of the cultivation broth could be partially compensated with the decrease in temperature, the latter mediated a major effect on CO_2 mass transfer.

C-CO_2 desorption ratios, defined as the ratio between the mass flow rate of IC desorbed from the cultivation broth and the total mass flow rate of IC supplied to the system (C-CO_2 absorbed in the absorption column + IC supplied in the centrate) and considering a carbon content of 50% in the microalgal biomass [30], of 51, 50, 2 and 4% were recorded in stages I, II, III and IV, respectively. However, a negligible C-CO_2 desorption was estimated at low alkalinities as a result of the low CO_2 mass transfer in the absorption column and low IC input via centrate addition, which ultimately resulted in process operation under carbon limiting conditions (Table 2). The highest CO_2 desorption rates obtained during stages I and II were associated to the high IC concentration in the cultivation broth, which supported a positive CO_2 concentration gradient to the atmosphere even though IC was mainly in the form of CO_3^{2-}. On the contrary, IC was preferentially used by microalgae rather than removed by stripping despite the low pH prevailing in the cultivation broth at low alkalinity. These results agreed with those reported by Meier et al. [19], who identified stripping as the main mechanism responsible for carbon removal in a 50 L photobioreactor fed with a mineral medium and connected to a bubble

Table 2
Inorganic carbon mass balance with the corresponding standard deviation (n = 4) under steady state conditions during the six operational stages tested.

Stage	Inputs ($g\,d^{-1}$)		Outputs ($g\,d^{-1}$)		
	IC biogas[a]	IC digestate[a]	IC biomass[a]	IC accumulated[a]	IC desorption[b]
I	7.87 ± 0.24	1.48 ± 0.20	4.54 ± 0.00	0.03 ± 0.04	4.78 ± 0.40
II	7.91 ± 0.61	1.37 ± 0.15	4.54 ± 0.00	0.02 ± 0.04	4.73 ± 0.70
III	4.04 ± 0.29	0.46 ± 0.04	4.54 ± 0.00	0.00 ± 0.00	0.11 ± 0.04
IV	4.20 ± 0.32	0.45 ± 0.05	4.54 ± 0.00	0.00 ± 0.00	0.20 ± 0.23
V	2.78 ± 0.46	0.08 ± 0.01	2.91 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
VI	3.78 ± 0.19	0.10 ± 0.01	3.93 ± 0.00	0.00 ± 0.00	0.00 ± 0.00

[a] Measured.
[b] Estimated from the mass balance.

column. Similarly, Alcántara et al. [10] observed a 49% CO_2 loss by desorption in a comparable 180 L HRAP interconnected to an absorption column during the simultaneous treatment of biogas and centrate.

3.2.2. H_2S-removal efficiency

Average H_2S-REs of 96.4 ± 2.9, 100 ± 0, 93.4 ± 2.6, 94.7 ± 1.9, 66.2 ± 6.9 and 80.3 ± 3.9% were recorded during stages I, II, III, IV, V and VI, respectively (Fig. 2). The higher H_2S-REs compared to CO_2-REs were attributed to the higher dimensionless Henry's Law constants of H_2S, defined as the ratio between the aqueous phase concentration of H_2S or CO_2 and its gas phase concentration ($H_{H2S} \approx 2.13$ and $H_{CO2} \approx 0.71$ at 20 °C) [27]. The highest H_2S removals were achieved at the highest alkalinities (stages I and II), corresponding to the highest pH along the absorption column. Similarly, Franco-Morgado et al. [18] obtained H_2S-RE of 99.5 ± 0.5% during the operation of a HRAP interconnected to an absorption column using a highly carbonated medium at a pH of 9.5. On the other hand, the low pH in the cultivation broth together with the large decrease in pH in the absorption column under low alkalinity caused the poor H_2S removal recorded (Table 1). These results were in accordance with those reported by Bahr et al. [6], who observed a significant deterioration in the H_2S-RE from 100% to 80% when the pH in the absorption column decreased from 7 to 5.4 in a similar HRAP-absorption column system.

No significant effect (t-student test, $p > 0.05$) of the temperature was observed at high-medium alkalinity on the removal of H_2S (Fig. 2). On the contrary, higher H_2S-REs were recorded at 12 °C under low alkalinity likely due to the increase in the aqueous solubility of H_2S.

H_2S oxidation ratios (defined as the mass flow rate of S-SO_4^{2-} accumulation in the HRAP divided by the mass flow rate of S-H_2S absorbed in the absorption column, subtracting the S-SO_4^{2-} introduced with the centrate) of 100%, 87% and 94% were obtained at 35 °C during stages I, III and V, respectively. However, an incomplete oxidation of H_2S occurred at 12 °C, resulting in ratios of 55%, 67% and 33% during stages II, IV and VI, respectively. The remaining sulfur being most likely present as S-intermediates (i.e. S°, thiosulfate or sulfite) or biomass (a typical S content of 0.07% can be assumed). Incomplete H_2S oxidation was also reported by Toledo-Cervantes et al. [3], who estimated than only 40% of the absorbed H_2S was oxidized to SO_4^{2-} in a similar experimental set-up. Interestingly, the high DO concentrations in the cultivation broth at 12 °C did not result in higher H_2S oxidation ratios likely due to the lower microbial activity at low temperatures.

3.2.3. Biomethane composition

An average CH_4 content of 98.9 ± 0.2, 98.2 ± 1.0, 80.9 ± 0.8, 82.5 ± 1.2, 75.9 ± 0.7 and 79.2 ± 0.7% was obtained in the final biomethane during stages I, II, III, IV, V and VI, respectively (Fig. 3). The high CH_4 contents in stages I and II (1500 mg IC L^{-1}) were attributed to the high absorption efficiency of CO_2 and H_2S and the limited desorption of N_2 and O_2. Furthermore, a negligible CH_4 absorption in the absorption column was observed along the six

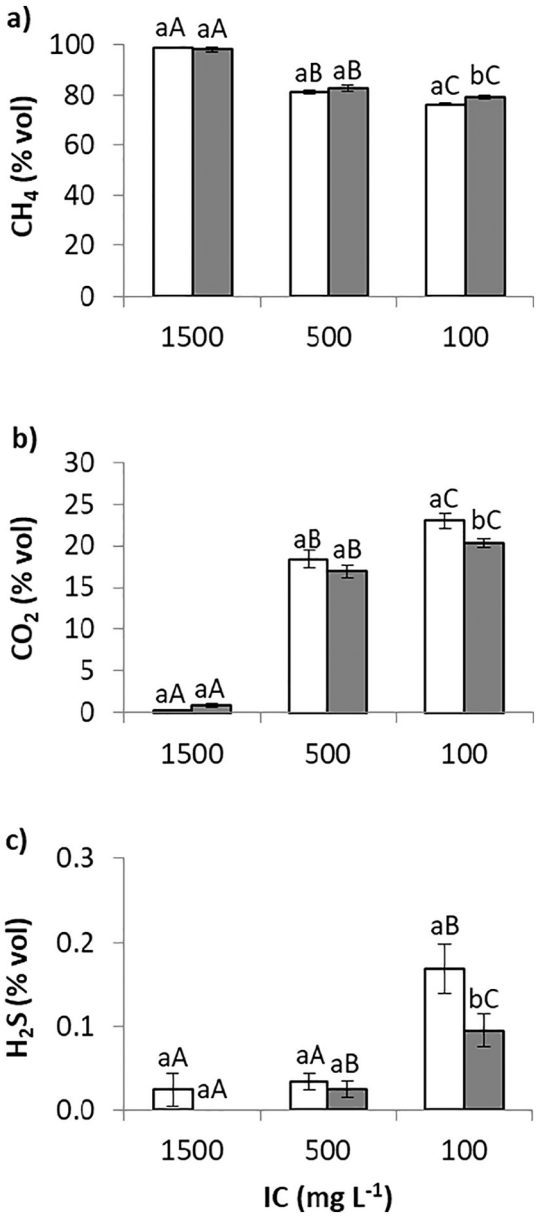

Fig. 3. Influence of the inorganic carbon concentration (IC) and temperature on bio-methane composition: a) CH_4, b) CO_2, c) H_2S average concentrations and their standard deviation (n = 8) at 35 °C (□) and at 12 °C (■). Same lowercase letters indicate not significantly different ($p > 0.05$) when compare both temperatures at each IC concentration. Same uppercase letters indicate no significantly different ($p > 0.05$) when compare the IC concentration for the same temperature.

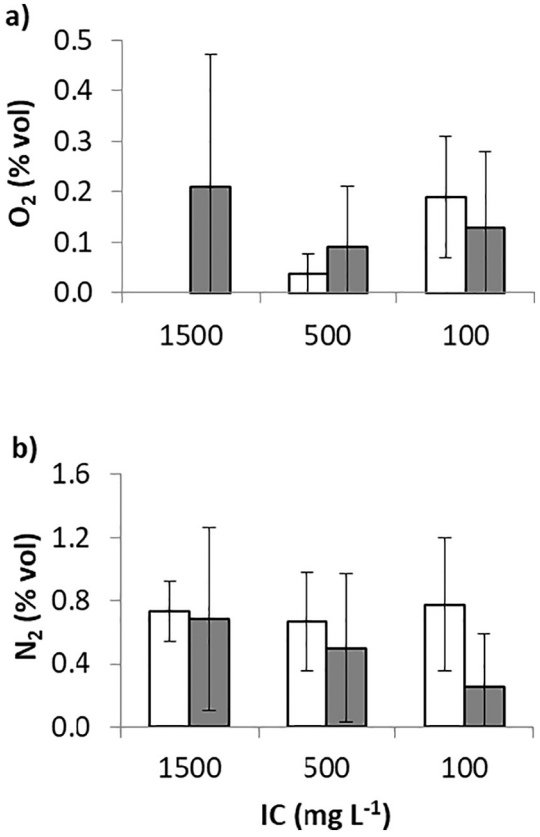

Fig. 4. Influence of the inorganic carbon concentration (IC) and temperature on bio-methane composition: a) O_2, b) N_2 average concentrations and their standard deviation (n = 8) at 35 °C (□) and at 12 °C (■). Average values were not significantly different during the six operational stages ($p > 0.05$).

operational stages, with average losses of 2.8 ± 3.4% (on a mass basis) regardless of the alkalinity or temperature. Posadas et al. [11] obtained slightly lower CH_4 losses (2.2 ± 1.2%) in an outdoors HRAP, while CH_4 losses of 4.9 ± 2.4% were reported by Toledo-Cervantes et al. [3] in a similar indoors system. At this point it should be pointed out that the composition of the biomethane produced in stages I and II complied with most European regulations for biogas injection into natural gas grids or use as autogas in terms of content of CH_4 (≥95%) and CO_2 < 2.5–4% [5]. In fact, the CO_2 content in the upgraded biogas accounted for 0.3 ± 0.1, 0.9 ± 0.3, 18.4 ± 1.0, 16.9 ± 0.8, 23.0 ± 0.9 and 20.3 ± 0.6% during stages I, II, III, IV, V and VI, respectively (Fig. 3).

During stages I to IV, H_2S concentrations below 0.03% were recorded in the upgraded biogas, which complied with EU regulations (Fig. 3). Moreover, no significant differences (One-way ANOVA, $p > 0.05$) in O_2 and N_2 content of the upgraded biogas were observed during the six operational stages (O_2 concentrations of 0.0 ± 0.0, 0.2 ± 0.3, 0.0 ± 0.0, 0.1 ± 0.1, 0.2 ± 0.1 and 0.1 ± 0.2%, and N_2 concentrations of 0.7 ± 0.2, 0.7 ± 0.6, 0.7 ± 0.3, 0.5 ± 0.5, 0.8 ± 0.4 and 0.3 ± 0.3% during stages I, II, III, IV, V and VI, respectively), which also matched the levels required by most European regulations (O_2 < 0.001–1%) (Fig. 4). These results might be explained by the low L/G ratio (0.5) applied during the study, which entailed a limited O_2 and N_2 stripping from the cultivation broth to the biomethane in the absorption column [18]. No significant effect of the microalgae population structure on the removals of CO_2 and H_2S, and on the stripping of N_2 or O_2, was expected above a certain photosynthetic activity threshold. In our particular study, the control of the biomass productivity (fixed at 7.5 $g\,m^{-2}\,d^{-1}$) guaranteed a constant rate of photosynthetic activity along the process regardless of the microalgae species dominant. In addition, previous works have consistently reported no-correlation between the dominant microalgae species and biogas upgrading performance [3, 8, 12].

4. Conclusions

The alkalinity of the cultivation broth was here identified as a key environmental parameter influencing biomethane quality. A negligible effect of the temperature on the quality of the upgraded biogas was recorded at high-medium alkalinity, while temperature played a significant role on biomethane quality at low alkalinity. Biomethane composition complied with most European regulations for biogas injection into natural gas grids or use as a vehicle fuel when photosynthetic biogas upgrading was carried out at high alkalinity (IC concentrations of > 1500 mg IC L^{-1}). In addition, this study also revealed that low alkalinity media might induce inorganic carbon limitation, which ultimately decreases the CO_2 mass transfer from biogas as a result of a rapid acidification of the scrubbing cultivation broth in the absorption column.

References

[1] C. Herrmann, N. Kalita, D. Wall, A. Xia, J.D. Murphy, Optimised biogas production from microalgae through co-digestion with carbon-rich co-substrates, Bioresour. Technol. 214 (2016) 328–337, http://dx.doi.org/10.1016/j.biortech.2016.04.119.
[2] E. Ryckebosch, M. Drouillon, H. Vervaeren, Techniques for transformation of biogas to biomethane, Biomass Bioenergy 35 (2011) 1633–1645, http://dx.doi.org/10.1016/j.biombioe.2011.02.033.
[3] A. Toledo-Cervantes, M.L. Serejo, S. Blanco, R. Pérez, R. Lebrero, R. Muñoz, Photosynthetic biogas upgrading to bio-methane: boosting nutrient recovery via biomass productivity control, Algal Res. 17 (2016) 46–52, http://dx.doi.org/10.1016/j.algal.2016.04.017.
[4] A. Toledo-Cervantes, J.M. Estrada, R. Lebrero, R. Muñoz, A comparative analysis of biogas upgrading technologies: photosynthetic vs physical/chemical processes, Algal Res. 25 (2017) 237–243, http://dx.doi.org/10.1016/j.algal.2017.05.006.
[5] R. Muñoz, L. Meier, I. Diaz, D. Jeison, A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading, Rev. Environ. Sci. Biotechnol. 14 (2015) 727–759, http://dx.doi.org/10.1007/s11157-015-9379-1.
[6] M. Bahr, I. Díaz, A. Dominguez, A. González Sánchez, R. Muñoz, Microalgal-biotechnology as a platform for an integral biogas upgrading and nutrient removal from anaerobic effluents, Environ. Sci. Technol. 48 (2014) 573–581, http://dx.doi.org/10.1021/es403596m.
[7] S. Sun, Z. Ge, Y. Zhao, C. Hu, H. Zhang, L. Ping, Performance of CO_2 concentrations on nutrient removal and biogas upgrading by integrating microalgal strains cultivation with activated sludge, Energy 97 (2016) 229–237, http://dx.doi.org/10.1016/j.energy.2015.12.126.
[8] M.L. Serejo, E. Posadas, M.A. Boncz, S. Blanco, P. García-Encina, R. Muñoz, Influence of biogas flow rate on biomass composition during the optimization of biogas upgrading in microalgal-bacterial processes, Environ. Sci. Technol. 49 (2015) 3228–3236, http://dx.doi.org/10.1021/es5056116.
[9] A. Xia, J.D. Murphy, Microalgal cultivation in treating liquid digestate from biogas systems, Trends Biotechnol. 34 (2016) 264–275, http://dx.doi.org/10.1016/j.tibtech.2015.12.010.
[10] C. Alcántara, P.A. García-Encina, R. Muñoz, Evaluation of the simultaneous biogas upgrading and treatment of centrates in a high-rate algal pond through C, N and P mass balances, Water Sci. Technol. 72 (2015) 150–157, http://dx.doi.org/10.2166/wst.2015.198.
[11] E. Posadas, D. Marín, S. Blanco, R. Lebrero, R. Muñoz, Simultaneous biogas upgrading and centrate treatment in an outdoors pilot scale high rate algal pond, Bioresour. Technol. 232 (2017) 133–141, http://dx.doi.org/10.1016/j.biortech.2017.01.071.
[12] A. Toledo-Cervantes, C. Madrid-Chirinos, S. Cantera, R. Lebrero, R. Muñoz, Influence of the gas-liquid flow configuration in the absorption column on photosynthetic biogas upgrading in algal-bacterial photobioreactors, Bioresour. Technol. 225 (2017) 336–342, http://dx.doi.org/10.1016/j.biortech.2016.11.087.
[13] E. Posadas, M.L. Serejo, S. Blanco, R. Pérez, P.A. García-Encina, R. Muñoz, Minimization of biomethane oxygen concentration during biogas upgrading in algal-bacterial photobioreactors, Algal Res. 12 (2015) 221–229, http://dx.doi.org/10.1016/j.algal.2015.09.002.
[14] G. Mann, M. Schlegel, N. Kanswohl, R. Schumann, Experimental system for the prevention of O_2^- and air contamination during biogas upgrading with phototrophic microalgae, Landbauforsch. Volkenrode. 66 (2016) 93–100, http://dx.doi.org/10.3220/LBF1471268642000.
[15] Y. Ouyang, Y. Zhao, S. Sun, C. Hu, L. Ping, Effect of light intensity on the capability of different microalgae species for simultaneous biogas upgrading and biogas slurry nutrient reduction, Int. Biodeterior. Biodegrad. 104 (2015) 157–163, http://dx.doi.org/10.1016/j.ibiod.2015.05.027.
[16] C. Yan, R. Muñoz, L. Zhu, Y. Wang, The effects of various LED (light emitting diode) lighting strategies on simultaneous biogas upgrading and biogas slurry nutrient

reduction by using of microalgae Chlorella sp, Energy 106 (2016) 554–561, http://dx.doi.org/10.1016/j.energy.2016.03.033.
[17] C. Yan, L. Zhu, Y. Wang, Photosynthetic CO_2 uptake by microalgae for biogas upgrading and simultaneously biogas slurry decontamination by using of microalgae photobioreactor under various light wavelengths, light intensities, and photoperiods, Appl. Energy 178 (2016) 9–18, http://dx.doi.org/10.1016/j.apenergy.2016.06.012.
[18] M. Franco-Morgado, C. Alcántara, A. Noyola, R. Muñoz, A. González-Sánchez, A study of photosynthetic biogas upgrading based on a high rate algal pond under alkaline conditions: influence of the illumination regime, Sci. Total Environ. 592 (2017) 419–425, http://dx.doi.org/10.1016/j.scitotenv.2017.03.077.
[19] L. Meier, P. Barros, A. Torres, C. Vilchez, D. Jeison, Photosynthetic biogas upgrading using microalgae: effect of light/dark photoperiod, Renew. Energy 106 (2017) 17–23, http://dx.doi.org/10.1016/j.renene.2017.01.009.
[20] R. Lebrero, A. Toledo-Cervantes, R. Muñoz, V. del Nery, E. Foresti, Biogas upgrading from vinasse digesters: a comparison between an anoxic biotrickling filter and an algal-bacterial photobioreactor, J. Chem. Technol. Biotechnol. 91 (2016) 2488–2495, http://dx.doi.org/10.1002/jctb.4843.
[21] E. Posadas, D. Szpak, F. Lombó, A. Domínguez, I. Díaz, S. Blanco, P.A. García-Encina, R. Muñoz, Feasibility study of biogas upgrading coupled with nutrient removal from anaerobic effluents using microalgae-based processes, J. Appl. Phycol. 28 (2016) 2147–2157, http://dx.doi.org/10.1007/s10811-015-0758-3.
[22] I. de Godos, H.O. Guzman, R. Soto, P.A. García-Encina, E. Becares, R. Muñoz, V.A. Vargas, Coagulation/flocculation-based removal of algal-bacterial biomass from piggery wastewater treatment, Bioresour. Technol. 102 (2011) 923–927, http://dx.doi.org/10.1016/j.biortech.2010.09.036.
[23] E. Posadas, P.-A. García-Encina, A. Soltau, A. Domínguez, I. Díaz, R. Muñoz, Carbon and nutrient removal from centrates and domestic wastewater using algal–bacterial biofilm bioreactors, Bioresour. Technol. 139 (2013) 50–58, http://dx.doi.org/10.1016/j.biortech.2013.04.008.
[24] M.A.H. Eaton, A.D. Clesceri, L.S. Rice, E.W. Greenberg, A.E. Franson, APHA: Standard Methods for the Examination of Water and Wastewater, Centen. ed., APHA, AWWA, WEF, Washington, DC, 2005.
[25] B. Guieysse, Q. Béchet, A. Shilton, Variability and uncertainty in water demand and water footprint assessments of fresh algae cultivation based on case studies from five climatic regions, Bioresour. Technol. 128 (2013) 317–323, http://dx.doi.org/10.1016/j.biortech.2012.10.096.
[26] E. Posadas, A. Muñoz, M.-C. García-González, R. Muñoz, P.A. García-Encina, A case study of a pilot high rate algal pond for the treatment of fish farm and domestic wastewaters, J. Chem. Technol. Biotechnol. 90 (2015) 1094–1101, http://dx.doi.org/10.1002/jctb.4417.
[27] R. Sander, Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, Last access: 12.11.2017, 1999. http://www.henrys-law.org/henry-3.0.pdf, .
[28] E. Molina, J. Fernández, F.G. Acién, Y. Chisti, Tubular photobioreactor design for algal cultures, J. Biotechnol. 92 (2001) 113–131, http://dx.doi.org/10.1016/S0168-1656(01)00353-4.
[29] O. Pulz, Photobioreactors: production systems for phototrophic microorganisms, Appl. Microbiol. Biotechnol. 57 (2001) 287–293, http://dx.doi.org/10.1007/s002530100702.
[30] Z. Arbib, J. Ruiz, P. Álvarez-Díaz, C. Garrido-Pérez, J.A. Perales, Capability of different microalgae species for phytoremediation processes: wastewater tertiary treatment, CO_2 bio-fixation and low cost biofuels production, Water Res. 49 (2014) 465–474, http://dx.doi.org/10.1016/j.watres.2013.10.036.