Anaerobic digestion of process water from hydrothermal carbonization of microalgae biomass

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Highlights

- Digestion of process water from 180 °C carbonization (PW180) had double methane yield than biomass
- PW240 showed lower methane production than biomass, possibly due to toxic compounds buildup
- Co-digestion resulted in higher production than separated sludge and PW240

Introduction

A-B process is a promising alternative for wastewater treatment with energy recovery. The A-stage is dedicated to organic matter (OM) capture and concentration and the B-stage to nutrient (mainly N, but also P) removal or recovery. Many technologies have been evaluated and combined for both stages, such as the chemical enhanced primary treatment (CEPT), very efficient for OM settling with coagulants aid, followed by microalgae cultivation, whose biomass assimilates macro and micronutrients while metabolizes the remaining OM (Vassalle et al., 2022). The cultivation of microalgae with submerged membranes, in so called membrane photobioreactors (MPBRs), is a very attractive approach to simultaneously increase biomass production and generate high-quality permeate that can be reused. In this new layout (CEPT followed by MPBR), the discharged biomass can later be used as a substrate for anaerobic digestion (AD), generating biogas, or for enhanced processes such as hydrothermal carbonization (HTC), where a carbonaceous material known as hydrochar is produced (Marin-Batista et al., 2019).

Hydrothermal carbonization is a thermochemical process for the treatment of biomass with high water content. Moreover, the process generates a carbonaceous solid named hydrochar, a liquid fraction called process water (PW) and a gas phase (Ipiales et al., 2021). The PW has been regarded as a difficult-to-manage by-product being the main drawback for the full-scale implementation of this technology. However, depending on the substrate used and the operational conditions of the process, the PW can be used as an anaerobic substrate for biogas production. Marin-Batista et al. (2019) studied the AD of PW obtained by HTC of microalgae biomass (180-240 °C) from a photobioreactor treating swine manure, obtaining higher methane yields from the PW than obtained from the raw biomass. This was attributed to the nature of microalgae cell walls, that were resistant to disruption and hindered the biodegradation of the cells content, but were breached and partially hydrolyzed during the HTC.

Moreover, other biological techniques can be evaluated to enhance methane production from PW, as the anaerobic co-digestion (AcoD) with other substrates (e.g. food waste, lignocellulosic biomass, sludges from wastewater treatment), looking for a circular economy. The AcoD of PW and primary sludge in an integrated system has been identified as a promising approach for enhancing biogas production (Villamil et al., 2020). AcoD is considered as a useful opportunity for enhancing methane production by balancing the carbon/nitrogen (C/N) ratio, diluting toxic compounds, and improving the balance of macro and micronutrients. However, a comprehensive investigation is necessary to optimize this process, considering also coagulants present in CEPT influence in AD (Thorin et al., 2018). The objective of this research was to evaluate the biochemical methane potential (BMP) of PW from the HTC of microalgae biomass generated in a membrane photobioreactor (MPBR) treating wastewater and integrated with CEPT. The co-digestion of the PW with the primary sludge was also evaluated to address the co-digestion effects on methane production.

Material and Methods

Figure 1 shows a scheme of the proposed integrated system to treat the affluent of a wastewater treatment plant (WWTP) of the University Autonoma of Madrid, Spain. The wastewater was subjected to CEPT with TANFLOC SG, a tannin-based coagulant modified by the Mannich reaction (Lamb and Decusati, 2002). A stock solution of 10 g·L^{-1} was prepared from the powdered tannin and an optimized dosage of 60 mg·L^{-1} was used, based on previous jar tests experiments. 5-liter beakers magnetically stirred were used for coagulation/flocculation process (C/F): initially, 1 min at 300 rpm, then 10 min at 50 rpm. The settle phase lasted for 1 h without stirring. The clarified supernatant was then used to feed the MPBR. Settled sludge and MPBR biomass were subjected to BMP assays. On the other hand, MPBR biomass settled for 1 h was stored in a freezer until HTC experiments were carried out.

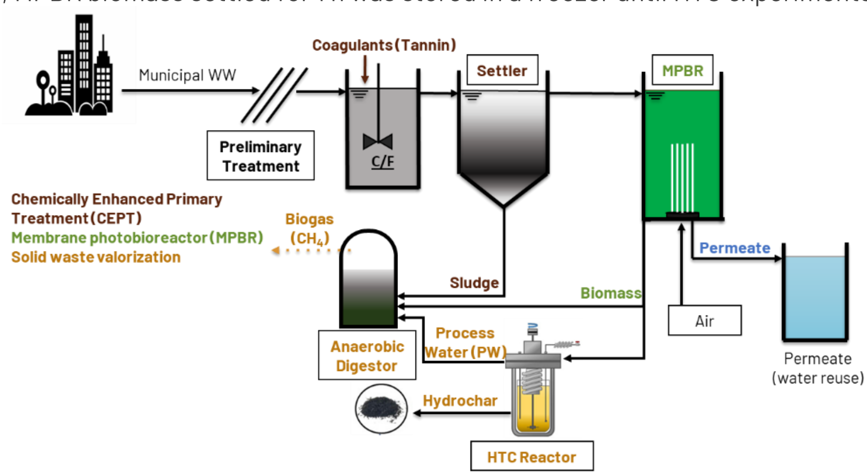

Figure 1 Schematic draw of the wastewater treatment system and waste valorization.

Hydrothermal carbonization was carried out in an agitated 2 L reactor (Parr Instrument, model 4524). The operating temperature (180 °C, 210 °C, and 240 °C) was reached and maintained for 1 h using a heating ramp of 4 °C·min^{-1} and a stirring speed of 200 rpm. The reaction was stopped by cooling at 10 °C·min^{-1} with an internal water coil. The reactor was loaded with 300 g of biomass (14.1 ± 0.2 g total solids (TS) ·kg^{-1} and 13.4 ± 0.1 g volatile solids (VS)·kg^{-1}). The total chemical oxygen demand (TCOD) of the biomass was 42.3 ± 0.5 g·L^{-1}. The slurry obtained after HTC was centrifuged and the PW samples, labelled considering the temperature used (PW180, PW210 and PW240), were stored in a fridge at 4 °C. Considering the sludge flow rate from a continuous treatment and the PW production, the volume ratio used in BMP for the AcoD assays was 7.5 L sludge:1 L PW. The sludge characteristics were 15.2 ± 0.1 g TS ·kg^{-1}, 13.7 ± 0.3 g VS ·kg^{-1} and 18.6 ± 0.3 g TCOD ·L^{-1}.

The BMP tests were carried out in hermetically sealed 120 mL flasks. The substrates were the MPBR biomass, PWs 180, 210 and 240, the CEPT sludge and a mixture of sludge and PW240, chose because of the better quality hydrochar produced in this HTC. The inoculum was granular sludge from an industrial digester processing brewery wastewater. The initial inoculum concentration was set at 10 g VS·L^{-1} and the inoculum-to-substrate ratio (ISR) employed was 2, on a VS basis. A nutrient solution (Villamil et al., 2018) and deionized water were also added to obtain a working volume of 60 mL. Nitrogen gas was sparged on the head space of the flasks to establish anaerobic conditions. The flasks were placed in a thermal water bath at 36 °C with shaking at 90 rpm.

The initial and final composition of the vials were analyzed in accordance with the standards outlined by the American Public Health Association (APHA, 2012). The analysis encompassed the assessment of TS, VS, soluble COD (SCOD), total ammoniacal nitrogen, pH, and alkalinity. The specific methods employed were 2540b, 2540d, 5220d, 4500NH_3, 4500H^+b, and 2310b.4c, respectively. The total COD was determined according to the method outlined by Raposo et al. (2008). Total Kjeldahl nitrogen (TKN) of the solid fraction was conducted in accordance with Villamil et al. (2018). The concentration of volatile fatty acids (VFA) was determined on a ShimadzuGC-230 instrument equipped with a flame ionization detector (FID) (Diez et al., 2024). Biogas production was assessed manometrically by measuring the pressure in each vial with a digital manometer (Sika) and expressed at standard temperature and pressure (STP: 273 K, 1 bar). Biogas composition (H_2, N_2, CO_2 and CH_4) was determined by GC separation on a Shimadzu GC-2014 unit equipped with a Carboxen 1010 PLOT fused silica capillary column and a thermal conductivity detector (TCD). Subsequently, the biogas was extracted from the flasks to restore atmospheric pressure. The experimental period was extended until methane production was undetectable or less than 5% of the total produced (on the last day).

Results and Discussion

Figure 2 shows the cumulative methane potential (A) and initial and final TCOD (B) of each sample tested. The methane production from each PW increases while the HTC temperature decreases; therefore, the PW240 presented the lowest production (88 ± 19 mL $CH_4 \cdot g^{-1}$ COD), even lower than with MPBR biomass (127 ± 15 mL $CH_4 \cdot g^{-1}$ COD), indicating the inhibition by toxic compounds that hindered the AD process. Meanwhile, the PW180 had almost the double of methane production (227 ± 5 mL $CH_4 \cdot g^{-1}$ COD). The methane yielded for PW210 (141 ± 2 mL $CH_4 \cdot g^{-1}$ COD) was similar to the reached for sludge (148 ± 4 mL $CH_4 \cdot g^{-1}$ COD). The co-digestion with PW240 improved the production compared to both substrates (198 ± 10 mL $CH_4 \cdot g^{-1}$ COD), indicating a synergistic effect. TCOD removal increased as the HTC temperature decreased, rising from 29% for PW240 to 39% for PW180. Meanwhile, the MPBR biomass achieved a COD removal of 58%. The AcoD process showed higher performance with 41% removal, compared to 29% for PW240 and 31% for sludge when treated separately.

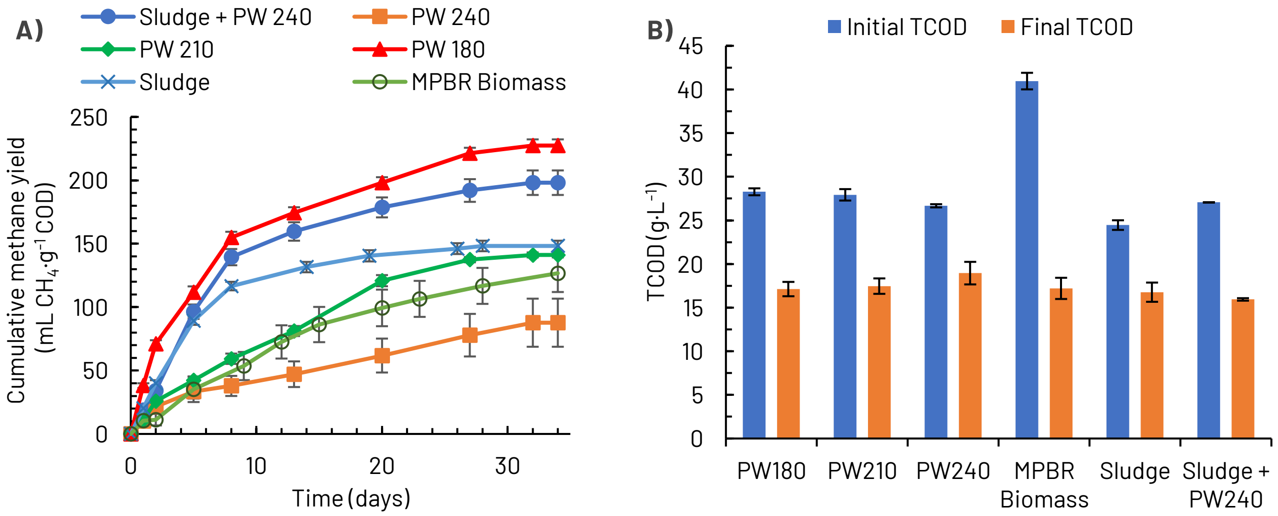

Figure 2 Cumulative methane potential (A) and initial and final TCOD (B) during BMP assays.

Table 1 shows the initial and final characterization of the samples tested. The pH of the samples ranged from 7.3 to 7.9, optimum for methanogenesis. Alkalinity above 2.5 g $CaCO_3 \cdot L^{-1}$ assure the necessary buffering capacity and was attained in all assays until their conclusion (Villamil et al., 2018). The TKN of the flasks with sludge, PW240 and their mixture ranged from 1.3 to 1.8 g $N \cdot L^{-1}$, and from 2.2 to 2.7 $g \cdot L^{-1}$ for the other substrates. Meanwhile, the ammoniacal nitrogen increased consistently from 0.2-0.4 $g \cdot L^{-1}$ at the beginning to 0.4-0.8 $g \cdot L^{-1}$ at the end of all assays, due to the conversion of organic nitrogen to ammonia, but remaining lower than inhibiting concentrations. Volatile solids removal followed a similar trend compared to TCOD variation and is also related to OM consumption in the process. It increased at diminishing HTC temperature from 14% for PW240 to 33% for PW 180, while MPBR biomass reached 31% removal, and AD or AcoD of sludge 26% and 24%, respectively.

Table 1 Values alkalinity, ammoniacal nitrogen, VS and SCOD from the anaerobic digestion experiments.

Substrate	Alkalinity ($mgCaCO_3 \cdot L^{-1}$)		$N\text{-}NH_3$ ($mg \cdot L^{-1}$)		VS ($g \cdot L^{-1}$)		SCOD ($mg \cdot L^{-1}$)		VFA ($mgCOD \cdot L^{-1}$)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
PW 180	1969 ± 158	4027 ± 78	331 ± 4	650 ± 9	14.6 ± 0.3	9.8 ± 0.3	5901 ± 290	132 ± 12	770 ± 11	51 ± 2
PW 210	2018 ± 88	3866 ± 23	377 ± 6	643 ± 6	13.8 ± 0.1	10.3 ± 0.1	5855 ± 241	304 ± 18	807 ± 22	69 ± 1
PW 240	2100 ± 96	3579 ± 86	379 ± 7	750 ± 28	12.0 ± 0.2	10.4 ± 0.1	6134 ± 241	5367 ± 319	1051 ± 4	2166 ± 59
MPBR Biomass	2081 ± 111	3649 ± 51	200 ± 10	655 ± 16	16.7 ± 1.0	12.0 ± 1.5	251 ± 14	369 ± 55	156 ± 7	85 ± 7
Sludge	1823 ± 82	3229 ± 29	215 ± 9	410 ± 6	13.5 ± 0.1	10.1 ± 0.1	651 ± 26	276 ± 8	238 ± 12	32 ± 1
Sludge + PW 240	1900 ± 58	4593 ± 177	226 ± 10	571 ± 47	13.8 ± 1.4	10.5 ± 0.2	767 ± 99	489 ± 24	592 ± 10	36 ± 1

average ± standard deviation.

Although the SCOD had much lower initial values for MBPR biomass and sludge (AD and AcoD) than for PWs, at the final of the assay all presented low values (< 500 $mg \cdot L^{-1}$), indicating organic matter conversion, except the assay with PW240, whose concentration remained high (5.4 $g \cdot L^{-1}$), which can be related to low methane production and the process inhibition. Process water, being the result of a hydrolysis process presenting high VFA initially, helped the fast biogas production observed especially for PW180. In these cases, although no VFA analysis was carried out during the assays, the final values lower than 100 mg COD·L^{-1} indicated a proper AD development. However, the accumulation for PW240 indicates a process unbalance, i.e., more acids are being produced than being consumed for methane production, which, associated with other factors, might be due to process inhibition (Marín-Batista et al., 2019; Villamil et al., 2018).

Conclusion

Anaerobic digestion of PW from the HTC of microalgae biomass is a viable strategy for biomass valorization and energy recovery from CEPT-MPBR process. Methane yields were highest for PW produced at lower HTC temperatures, while higher temperatures led to lower biodegradability and the accumulation of inhibitory compounds. Co-digestion of PW with CEPT sludge significantly enhanced methane production compared to each substrate alone, indicating a synergistic effect. These findings highlight the importance of optimizing HTC conditions and co-digestion strategies to maximize energy recovery and process sustainability. Further research is needed to characterize inhibitory compounds in PW and to validate these results at continuous scale for future industrial implementation.

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