Research Paper

Enhancement of biogas production rate from bioplastics by alkaline pretreatment

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ABSTRACT

The effect of alkali-based pretreatment on the methanization of bioplastics was investigated. The tested bioplastics included PHB [poly(3-hydroxybutyrate)], PHBH [poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)], PHBV [poly(3-hydroxybutyrate-co-3-hydroxyvalerate], PLA (polylactic acid), and a PLA/PCL [poly(caprolactone)] 80/20 blend. Prior to methanization tests, the powdered polymers (500–1000 μm) at a concentration of 50 g/L were subjected to alkaline pretreatment using NaOH 1 M for PLA and PLA/PCL, and NaOH 2 M for PHB-based materials. Following 7 days of pretreatment, the amount of solubilized carbon for PLA and its blend accounted for 92–98% of the total initial carbon, while lower carbon recoveries were recorded for most PHB-based materials (80–93%), as revealed by dissolved total organic carbon analysis. The pretreated bioplastics were then tested for biogas production by means of mesophilic biochemical methane potential tests. Compared to unpretreated PHBs, methanization rates of pretreated PHBs were accelerated by a factor of 2.7 to 9.1 with comparable (430 NmL CH_4/g material feed) or slightly lower (15% in the case of PHBH) methane yields, despite featuring a 1.4–2.3 times longer lag phases. Both materials, PLA and the PLA/PCL blend, were only extensively digested when pretreated, yielding about 360–380 NmL CH_4 per gram of material fed. Unpretreated PLA-based materials showed nearly zero methanization under the timeframe and experimental conditions tested. Overall, the results suggested that alkaline pretreatment can help to enhance the methanization kinetics of bioplastics.

1. Introduction

Nowadays, there is an increasing interest in the production and deployment of bioplastics owing to their versatile, tailor-made properties and applications, along with the fact that they help reducing the demand of fossil fuels, have a smaller carbon footprint than their petroleum-derived counterparts, and some of them are biodegradable under appropriate environments and time frames (Cucina et al., 2021; Van Roijen and Miller, 2022). Over the last decade, the global production capacity of bioplastics has increased from 1.4 up to 2.4 million tonnes in 2021, and their market share is forecast to reach a 3-fold increment by 2026 (European Bioplastics, 2022). Due to such an expected rapid growth, the development and widespread implementation

of efficient bioplastic waste management technologies is of utmost importance to build a more sustainable and circularity-oriented bioplastics industry (Folino et al., 2020; García-Depraect et al., 2021; Van Roijen and Miller, 2022).

The end-of-life (EOL) management scenarios for bioplastics include mechanical recycling, chemical recycling, and organic recycling such as industrial composting and anaerobic digestion (AD) (García-Depraect et al., 2021). The appropriate EOL option is mainly dependent on the features and applications of a given polymer, its level of contamination, as well as the nearby infrastructure availability (TotalEnergies Corbion, 2020). Policy measures can also help reducing bioplastics waste and increasing recycling rates. A good example of an environmental policy approach that can be adopted by the bioplastics sector is the Extended

producer responsibility (EPR) scheme, in which a producer's responsibility for a product is extended to the post-consumer stage of a product's life cycle (OECD, 2022). The Italian Biorepack consortium, which is claimed as the first EPR scheme in Europe for the organic recycling of biodegradable and compostable plastic packaging sector, reported that in 2021 about 38,400 tonnes of biodegradable and compostable plastic packaging (corresponding to 52% of the total yearly amount consumed) were organically recycled (Biorepack, 2022). Thus, the biodegradable nature of some bioplastics allows for organic recycling (i.e., composting and AD) and other emerging upcycling biotechnologies based on the use of enzymes and microorganisms to produce high-value chemicals (García-Depraect et al., 2021; Blank et al., 2020).

AD is a 4-stage degradation bioprocess (i.e., hydrolysis, acidogenesis, acetogenesis, methanogenesis) in which organic matter is anaerobically transformed mainly into biogas [a mixture of carbon dioxide (CO_2) and methane (CH_4)] by the coordinated action of multiple microorganisms including anaerobic bacteria and methanogenic archaea. From an energy point of view, AD has been demonstrated as a valuable disposal option for bioplastic bags containing bio-waste and other bio-waste-contaminated bioplastics, which allows carbon and nutrients recycling while producing biogas as a renewable energy carrier and a digestate that can be used as soil biofertilizer (Bátori et al., 2018). As highly carbon-rich materials, bioplastics can be co-digested with feedstocks having lower C/N ratios such as agricultural residues, food wastes, manures, wastewater sludge, among others (Abraham et al., 2021). In this context, the potential anaerobic biodegradability of bioplastics is impacted not only by their physical–chemical features but also by the microbial diversity and environmental and operational conditions involved (Abraham et al., 2021). It must be stressed that not all types of bioplastics can be efficiently managed by AD (Bátori et al., 2018). The family of polyhydroxyalkanoates (PHAs) polyesters, polylactic acid (PLA), and poly(caprolactone) (PCL) are among those that have been found to be susceptible to anaerobic biodegradation (Bátori et al., 2018). However, efficient AD of bioplastics is still quite challenging since most bioplastics exhibit too low hydrolysis rates due to their polymeric composition and morphology (Yasin et al., 2022).

The degradation time of biodegradable bioplastics is typically 3 to 6 times longer than the typical hydraulic retention time (HRT; 15–30 days) of municipal biogas plants (Bátori et al., 2018; Cazaudehore et al., 2023; García-Depraect et al., 2022a; Narancic et al., 2018; Shrestha et al., 2020). Therefore, the application of efficient and cost-effective pretreatments can boost the AD of bioplastics in order to be successfully biodegraded in a suitable timeframe. Bioplastic pretreatment is intended to enhance the extent and rate of biodegradation by providing low molecular weight fragments or single monomers from complex polymers and/or modifying the physical–chemical characteristics (e.g., crystallinity, molecular mass, specific surface area) of bioplastic products (García-Depraect et al., 2021). However, the number of systematic studies focussed on the use of bioplastics pretreatments remains yet very limited (see recent review by Yasin et al., 2022). Alkaline pretreatment is among the most promising bioplastics pretreatments for improving biodegradation, mostly via hydrolysis (Yasin et al., 2022; Yu et al., 2005). Indeed, the hydrolysis efficiency (in terms of the amount of carbon solubilized from bioplastic material) of alkali-based pretreatments is relatively high (70% on average) for PHAs and higher than 90% in the case of PLA (Yasin et al., 2022). Nonetheless, despite alkaline pretreatment (often in combination with mechanical grinding and high temperatures) has been proven to be effective in boosting abiotic bioplastic degradation, its integration with AD remains less well studied for various bioplastics (Battista et al., 2021; Benn and Zitomer, 2018; Calabro' et al., 2020; Cazaudehore et al., 2022a; Samitthiwetcharong and Chavalparit, 2019). Hence, the present study aims at investigating the effect of alkaline pretreatment on the AD of five commercial bioplastics, namely, poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), PLA, and a PLA/PCL [poly(caprolactone)] blend. Particular attention was given to the assessment of the pretreatment hydrolysis efficiency and the kinetics of methanization through biochemical methane potential (BMP) assays.

2. Materials and methods

2.1. Polymers

The polymers tested for alkaline pretreatment and further methanization were obtained from the following commercial trade brands: PHB (ENMAT™ Y3000P), PHBH (Danimer), PHBV [ENMAT™ Y1000P, 3 mol% HV (hydroxyvalerate)], PCL (Capa® 6500D), PLA (LUMINY® L105), and PLA/PCL 80/20 blend (PLA Luminy® L105/PCL Capa® 6500D). All the bioplastics were purchased from ITENE (Technological Institute of Packaging, Transportation and Logistics) in Spain. Initially, each bioplastic in pellet form was mechanically grinded with dry ice and then sieved to obtain a powder sample with a particle size between 500 and 1000 μm, following the procedure reported elsewhere (García-Depraect et al., 2022b). Finally, the powdered bioplastics were dried at room temperature and separately stored in a dry place away from sunlight.

2.2. Alkaline pretreatment

Monobasic sodium hydroxide (NaOH) is well-known to be one of the most effective alkali agents for increasing the specific surface area and depolymerizing biomass (Vu et al., 2020). A screening evaluation of alkaline pretreatment was initially carried out to investigate the influence of NaOH concentration and type of bioplastic on carbon solubilization. The pretreatment was performed for 15 or 25 days (depending on the bioplastic type) in 250-mL borosilicate bottles (with 100 mL working volume) at four different bioplastic concentrations, i.e., 50, 100, 150 and 200 g/L. The bottles were sealed using screw caps, incubated at 37 ± 1 °C, and continuously mixed by magnetic stirring at 100 rpm. The amount of organic carbon that is solubilized from each powdered polymer was tracked over time as soluble total organic carbon (TOC). All bioplastics were directly soaked in NaOH solution. For all the bioplastics tested, alkaline pretreatment started using NaOH 1 M. However, the alkali concentration was later increased to 3 M (except in the case of PHBH whose NaOH concentration remained at 1 M), as a measure to further increase the hydrolysis efficiency, as recommended by Siddiqui et al. (2021) and Yu et al. (2005). The decision of increasing NaOH concentration was made based on the behaviour observed in carbon solubilization. Particularly, the concentration of alkali was increased from 1 M to 3 M only when a given material showed a constant and comparatively lower TOC concentration (than the maximum achievable value) over time. The efficiency of hydrolysis (η_{hyd}), defined as the amount of carbon solubilized referred to the total carbon initially contained in the polymer, was estimated according to Eq. (1). Analytical-reagent grade NaOH was purchased from Labkem (Spain).

Based on the findings observed during the screening assessment, a new experimental set of alkaline pretreatments was carried out for one week in 250-mL borosilicate bottles with a working volume of 100 mL and 5 g total solids, corresponding to a bioplastic loading of 50 g/L. NaOH 1 M was the alkali solution used for PLA and the PLA/PCL blend, and NaOH 2 M for PHB, PHBH, and PHBV. The bottles were sealed, incubated, and stirred at the same conditions described above. Controls with deionized water were performed in parallel. At the end of the pretreatment, liquid samples were collected and analysed for soluble TOC and pH. The pH of the pretreated bioplastic suspensions was neutralized using concentrated HCl (37%) before further methanization.

$$\eta_{hyd}(\%) = \frac{[\text{Final soluble TOC}]\,(g)}{[\text{Carbon}_{polymer}]\,(g)} \times 100 \qquad (1)$$

2.3. Biochemical methane potential (BMP) tests

A series of BMP tests was carried out to investigate the effect of alkaline pretreatment on the extent and rate of the bioplastics methanization. The BMP assays were conducted in 2.1-L screw-cap glass bottles with a working volume of 1 L. Initially, each bottle was fed with the needed amount of pretreated bioplastic suspension to a polymer loading of 1 g/L. Then, the bottles were filled with 500 mL of a mineral medium composed of (in g/L): $Na_2HPO_4·12H_2O$, 5.6; KH_2PO_4, 1.35; NH_4Cl, 0.53; $MgCl_2·6H_2O$, 0.1; $Na_2S·9H_2O$, 0.1; $CaCl_2·2H_2O$, 0.075; $FeCl_2·4H_2O$, 0.02; resazurin, 0.001 (modified from García-Depraect et al., 2022a). All reagents were of analytical grade. The bottles were inoculated with anaerobic sludge kindly supplied by the wastewater treatment plant of Valladolid, Spain, and filled up to 1 L with the mineral medium described above. The food to microorganism (F/M) ratio was fixed at 2 [on a volatile solids (VS) basis], which is among the recommended values for AD (Neves et al., 2004). The seeding sludge was not used as received but preincubated for 6 days at 36 ± 1 °C under anaerobic conditions to reduce background biogas production during the BMP assays (García-Depraect et al., 2022b). Finally, the bottles were capped tightly with a butyl rubber stopper and an aluminium screw cap, flushed with helium gas (Abello Linde, Barcelona, Spain) for 5 min, and incubated under gentle agitation (4.5 rpm) in a Wheaton roller apparatus (Scientific Products, USA) placed in a 37 ± 1 °C constant temperature room. Unpretreated powdered polymers with a particle size of 500–1000 μm were used as the control for the sake of comparison. A blank assay was also performed to measure endogenous biogas production. Additionally, a positive control was run in parallel with microcrystalline cellulose (Merck Ltd., Germany, CAS number 9004–34–6). All experimental conditions were tested in triplicate.

Weekly measurements of biogas production were recorded by a standard manometric method (García-Depraect et al., 2022a). The BMP tests ended when the cumulative biogas production curve plateaued. Biogas volume was normalized to standard temperature and pressure conditions (0 °C and 1 atm). Methane yield was expressed as the volume of CH_4 per gram of VS fed. The time course of methane yield was modelled by the modified Gompertz model (Diaz-Cruces et al., 2020). At the end of the experiment, samples of the digestate were collected and analysed for pH, volatile organic acids (VFAs), dissolved inorganic carbon (DIC) and soluble TOC. The final degree of biodegradation was calculated by comparing the total net mass of gaseous carbon (CH_4 and CO_2) and net DIC (mass of DIC at the end of incubation for the tested material minus that recorded from the blank) with the mass of bioplastic carbon initially fed to the tests (García-Depraect et al., 2022a). Finally, a carbon mass balance analysis was performed to elucidate bioplastic carbon fate during AD, i.e., CO_2, CH_4, DIC, soluble TOC. The carbon flow diverted towards biomass growth was assumed to be 10% of the total initial carbon fed (Chernicharo, 2007). One way analysis of variance (ANOVA) at 95% confidence level was used to determine significant differences among the data collected.

2.4. Analytical procedures

Biogas composition was determined by gas-chromatography using a thermal-conductivity-detection (GC-TCD) method, as previously reported elsewhere (García-Depraect et al., 2022a). A pressure transducer (IFM electronic PN7097, Germany) was used to record the headspace pressure in the BMP bottles. VFAs were measured in centrifuged (10000 rpm for 10 min), filtered (0.22 μm) and acidified (using concentrated sulfuric acid) samples by gas-chromatography using a flame-ionization-detection (GC-FID) method, as reported by García-Depraect et al. (2022b). Total and volatile solids concentrations and pH were analysed according to standard methods (APHA, 2005). DIC and dissolved TOC were measured by a total organic carbon analyser (Shimadzu TOC-VCSH, Japan) in samples previously centrifuged (10000 rpm for 10

min) and filtered (0.45 μm). Crystallinity of materials was measured via differential scanning colorimetry (DSC), as previously reported by Santos-Beneit et al., 2023.

3. Results and discussion

3.1. Alkaline pretreatment

An initial screening assay was conducted to determine the optimal alkaline pretreatment conditions. The assay consisted of monitoring the amount of organic carbon that was solubilized from each powdered polymer over time, at two NaOH (1 vs. 3 M) and four different polymer concentrations (50, 100, 150 and 200 g/L). As shown in Fig. 1, at the lowest bioplastic concentration of 50 g/L, 1 M NaOH was high enough (0.8 g NaOH/g polymer) to support high carbon solubilization yields (95–100%) within the first 3 and 10 days of pretreatment for PLA- and most PHB-based materials, respectively. Contrarily, higher bioplastic concentrations (>50 g/L) required higher NaOH concentrations to achieve enhanced hydrolysis efficiencies regardless of the type of material. Thereby, PLA and the blend composed of 80% PLA and 20% PCL were comparatively more susceptible to be hydrolysed via alkaline pretreatment than PHBs. At the end of the pretreatment, 98 to 100% of the initial carbon contained in PLA was solubilized, while the pretreated PLA/PCL material reached a carbon solubilization yield of 93–100% (Fig. 1f). Such high hydrolysis efficiencies recorded for PLA are in good agreement with those reported in literature (Hobbs et al., 2019; Samitthiwetcharong and Chavalparit, 2019). However, to the best of our knowledge, this is the first study reporting the alkaline pretreatment of a PLA/PCL blend, although it has been reported that PCL structure can be vulnerable to alkaline hydrolysis (Meseguer-Dueñas et al., 2011).

An unexpected finding in the present study is that a comparison of the hydrolysis rates recorded for PHBs at 50 g/L revealed that PHBH was the most difficult to be pretreated, while PHB and PHBV exhibited very similar behaviours (Fig. 1c–d). Typically, PHBH features lower crystallinity as it contains long-side-chain monomers of 3-hydroxyhexanoate which reduces crystallinity. The crystallinity of PHBH decreases with the increase in the 3-hydroxyhexanoate (3HH) content, which may result in an accelerated biodegradation rate (Eraslan et al., 2022). PHBs in-depth analysis of crystallinity via DSC in the powdered polymers revealed that PHB and PHBV shared a similar degree of crystallinity (58%) while the PHBH copolymer, which has shown enhanced mechanical properties compared to PHB and PHBV (Eraslan et al., 2022), exhibited a slightly lower crystallinity value (44%).

Based on the above findings, the bioplastics were pretreated for 7 days using a bioplastic concentration of 50 g/L and NaOH doses of 1 M and 2 M for PLA-made materials and PHB-based materials, respectively, before conducting the BMP tests. At the end of the pretreatment, the final pH values of the reaction mixture were about 12.7 for the PLA-based bioplastics and 13.0 for the PHBs. The final hydrolysis efficiencies at day 7 accounted for 92, 98, 93, 86 and 80% for PLA, PLA/PCL, PHB, PHBV and PHBH, respectively. Although at the expense of requiring higher energy inputs, the relatively longer pretreatment time herein tested could be shortened without jeopardizing, in fact, rather improving the hydrolysis yields by thermo-alkaline pretreatment, as demonstrated by other studies (Table 1).

Sequential alkali pretreatment and AD has been widely applied for the valorization of lignocellulosic biomass, which besides promoting delignification causes the swelling of cellulose fibers, leading to a reduction in their crystallinity and degree of polymerization (Kumari and Das, 2015; Zhu et al., 2010). However, the alkaline pretreatment-aided AD approach applied to bioplastics has been much less investigated (Cazaudehore et al., 2022b; García-Depraect et al., 2021; Yasin et al., 2022). Under alkaline conditions, hydroxide ions can promote polymer hydrolysis via ester cleavage without risk of re-esterification due to thermodynamic barriers, thus facilitating the decomposition of the polymer backbone via surface- and/or bulk-erosion mechanism into
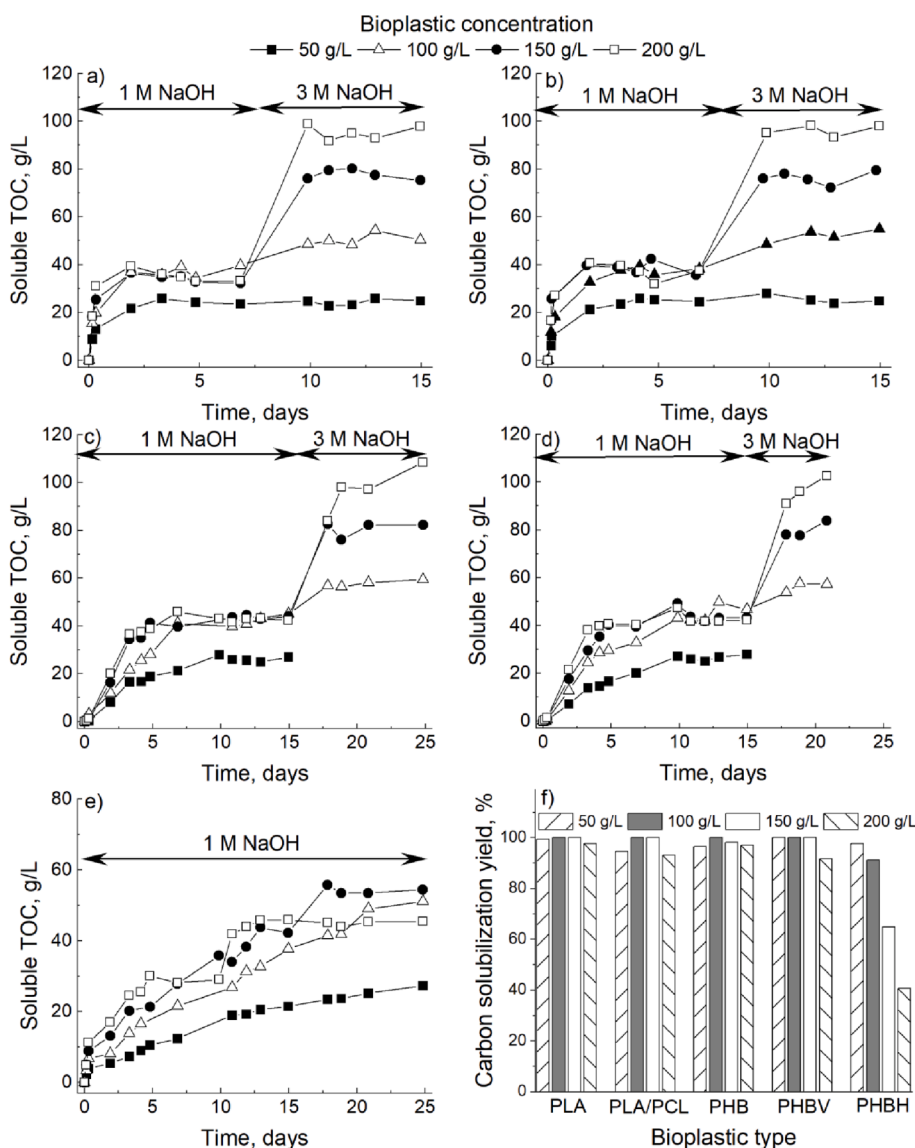
Fig. 1. Time course of soluble TOC released during alkaline pretreatment for a) PLA, b) PLA/PCL blend, c) PHB, d) PHBV and e) PHBH. f) Final carbon solubilization yield achieved for the different types and concentrations of bioplastics. Alkaline pretreatment started with a NaOH concentration of 1 M, which was increased to 3 M in some cases (a–d), depending on the amount of solubilized carbon observed. Horizontal arrows indicate the time of pretreatment applied with a NaOH concentration of either 1 M or 3 M.

Table 1
Comparison of bioplastics decomposition by alkaline pretreatment reported in literature.

Bioplastic type	Alkali Conc. and temperature	Polymer Conc. (g/L)	Treatment duration	Hydrolysis efficiency (%)	Reference
PLA pellets (80 μm thickness 1–2 mm size)	NaOH 0.5 M (ambient temp.)	100	60 h	36 (18.2 g lactic acid/L)	(Samitthiwetcharong and Chavalparit, 2019)
Thin-film amorphous PLA bags & crystalline PLA cups (both 2 × 2 cm)	NaOH 10 M (21 ± 1 °C)	N.R.	15 days	97–99	(Hobbs et al., 2019)
Native PHB granules	NaOH 4 M (70 °C)	20	4 h	70	(Yu et al., 2005)
PHBV (5 mol% 3HB)	NaOH 0.1 M (pH 13, 60 °C)	1.2	18 h	98	(Myung et al., 2014)
PLA (500–1000 μm)	NaOH 1 M (37 °C)	50	1 week	92	Present study
PLA/PCL (500–1000 μm)	NaOH 1 M (37 °C)	50	1 week	98	Present study
PHB (500–1000 μm)	NaOH 2 M (37 °C)	50	1 week	93	Present study
PHBV (500–1000 μm)	NaOH 2 M (37 °C)	50	1 week	86	Present study
PHBH (500–1000 μm)	NaOH 2 M (37 °C)	50	1 week	80	Present study

N.R.: not reported.

soluble monomers (and/or oligomers), such as 3-hydroxybutyric acid and crotonic acid from PHB and lactic acid from PLA (Samitthiwetcharong and Chavalparit, 2019; Yu et al., 2005).

3.2. Impact of alkaline pretreatment on bioplastics methanization

A series of BMP tests was performed to investigate the impact of alkaline pretreatment on bioplastics methanization. The BMP tests were carried out with pretreated and unpretreated bioplastics as the

substrate, and anaerobic sludge not previously exposed to bioplastics as the inoculum. As shown in Fig. 2a, the methane yield of microcrystalline cellulose (positive control) following 57 days of incubation was 344 ± 10 NmL CH_4/g VS_{fed}, which corresponds to 82.9 ± 2.4% of the maximum theoretical yield, thereby validating the good quality of the inoculum used in the assays (Holliger et al., 2016). The cumulative production of methane (normalized to gram of VS fed) recorded as a function of time for all the pretreated bioplastics and their corresponding unpretreated controls is shown in Fig. 2a–e. The time courses of cumulative methane production were successfully modelled using the modified Gompertz model. A visual inspection of the predicted data and the kinetic parameters of the model, i.e., λ (lag phase), *Pmax* (maximum methane potential) and *Rmax* (maximum methane production rate), are presented in Fig. 2 and Table 2, respectively.

Significant lag phases were observed under all experimental conditions tested. In this context, alkaline pretreatment significantly delayed the onset of biogas production. As shown in Table 2, the length of the lag phases occurring in the pretreated PHBs tests were on average between 19.9 and 23.7 days, which were 1.4–2.3 times longer than those recorded in the non-pretreated PHBs tests but similar to that reported for the methanization of PHB under thermophilic conditions (Cazaudehore et al., 2023). The here investigated bioplastics, specifically PHAs caused a significant delay in methanization (i.e., increased lag-phase) as compared to other biopolymers, such as cellulose hardly featuring any onset in methanization (see Fig. 2a). Interestingly, pretreated PLA-based materials started to produce biogas almost immediately, a very different behaviour than that of PHB-based materials, which agrees well with previous observations of PLA methanization (Cazaudehore et al.,

Table 2
Summary of the modified Gompertz model's kinetic parameters obtained for the different bioplastics tested.

Material	λ (days)	*Pmax* (NmL CH_4/g VS_{fed})	*Rmax* (NmL CH_4/L-day)	R^2
Pretreated PHB	a 20.3 ± 0.3	a 419.2 ± 9.1	a 59.5 ± 14.2	0.9990
Unpretreated PHB	b 13.1 ± 1.2	b 452.5 ± 13.4	b 10.6 ± 0.4	0.9954
Pretreated PHBH	a 19.9 ± 0.1	a 407.2 ± 19.7	a 42.5 ± 0.9	0.9978
Unpretreated PHBH	b 13.7 ± 1.2	b 463.6 ± 18.9	b 15.3 ± 3.1	0.9963
Pretreated PHBV	a 23.7 ± 1.7	a 435.5 ± 12.9	a 86.2 ± 22.6	0.9992
Unpretreated PHBV	b 10.0 ± 4.8	b 476.3 ± 14.4	b 9.5 ± 0.6	0.9952
Pretreated PLA	3.9 ± 1.6	385.5 ± 1.6	14.8 ± 1.4	0.9805
[1]Unpretreated PLA	–	–	–	–
Pretreated PLA/PCL	5.6 ± 0.4	408.5 ± 10.0	16.5 ± 0.4	0.9902
[1]Unpretreated PLA/PCL	–	–	–	–

A statistical comparison (one-way ANOVA) between the unpretreated and pretreated conditions was performed by type of bioplastic; for a specific bioplastic, same letter within a column indicates that values are not significantly different at p-value ≤ 0.05. [1] Unpretreated PLA-based materials were not subjected to modelling as these materials resulted in negligible amounts of methane.
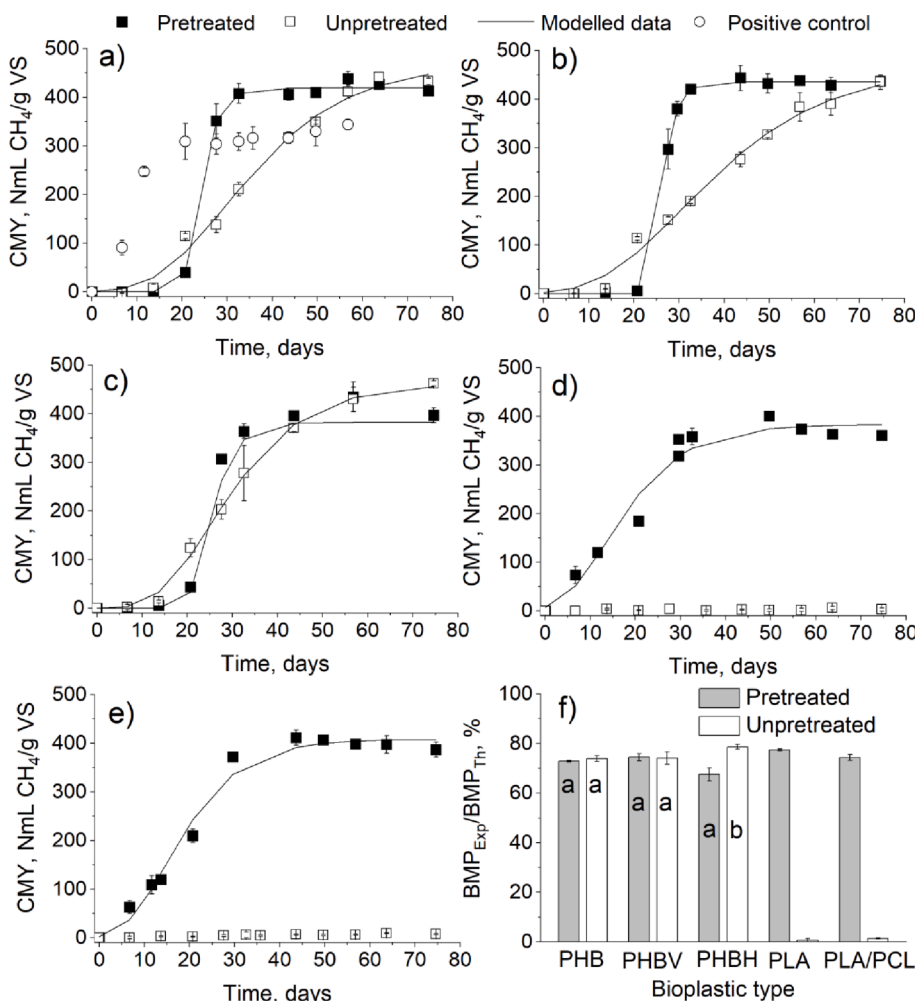

Fig. 2. Time course of cumulative methane yield (CMY) for alkaline pretreated and untreated a) PHB, b) PHBV, c) PHBH, d) PLA, and e) PLA/PCL blend. The bar graph f) shows a comparison of the ratio between the experimental methane yield (BMP_{EXP}) computed for pretreated and unpretreated bioplastics at the end of the experiment and its corresponding theoretical methane yield (BMP_{Th}). Different letters for a specific type of PHB indicate that alkaline pretreatment affected significantly (p-value ≤ 0.05) the final methane yield. The methanization of the positive control (microcrystalline cellulose) is also shown in a) as empty circles.

2022a). It is well accepted that during the lag phase (the time that precedes the beginning of exponential biogas production), bioplastics are hydrolysed into soluble molecules before further degradation occurs (García-Depraect et al., 2021). It has been reported that AD might be negatively affected by the presence of high cations concentrations from the reagents employed in chemical pretreatments, like sodium in the case of NaOH (Ariunbaatar et al., 2014; Battista et al., 2021). In contrast, the concentration of sodium in the BMP tests with pretreated PHBs and PLA-made polymers was estimated to be 1.6 and 1.1 g/L, respectively, while that in the tests with unpretreated bioplastics was about half the value, i.e., 0.7 g/L. Ionic strength-induced inhibition was considered unlikely, as those sodium concentrations were considerably below the reported inhibition threshold levels (5 g/L) for methanogenesis (Ariunbaatar et al., 2014). Thus, it remains unclear why the pretreated PHB-based materials experienced an extended delay in biogas production. Perhaps such a consistent trend would be more related to the physiological and/or molecular responses of microorganisms to the different nature of substrates (monomers) involved, where lactic acid released from PLA-based materials seems to be metabolized into biogas more rapidly than the soluble monomers (and/or oligomers) potentially released from PHBs. That might explain why no pronounced lag phase was observed for PLA-based materials, while all PHAs tested herein seemed to behave rather similar. Transient inhibition issues could be another explanation for the increased lag phases observed, which needs further confirming studies. Nonetheless, these time delays in biodegradation due to the extended lag periods observed can be overcome by operating continuous co-digesters (treating food waste for instance), which besides allowing biomass adaptation can simultaneously dilute the cations contained in the alkaline reagent.

Examination of the methane yields recorded experimentally for pretreated and unpretreated materials following incubation showed that alkaline pretreatment did not significantly affect the methane potential, except in the case of pretreated PHBH which exhibited a slightly lower degree of methanization than its unpretreated control (Fig. 2). Here it should be noted that the estimated *Pmax* values (methane potential) obtained from modelling showed that unpretreated PHB-based materials exhibited a superior methane yield compared to those of their corresponding pretreated materials (Table 2). However, this contradictory trend resulting from the analysis of experimental and predicted data should be interpreted with care since there was an overestimation of the ultimate methane potential of unpretreated PHB-based bioplastics, likely due to the lack of fit for stationary phases. After 75 days of AD, the methane yields of unpretreated bioplastics were (in NmL CH_4/g VS_{fed}) 432.7 ± 6.7 (PHB), 435.1 ± 15.0 (PHBV), 462.3 ± 5.5 (PHBH), 3.1 ± 2.9 (PLA), 7.4 ± 1.2 (PLA/PCL). The corresponding methane yields for pretreated bioplastics were (in NmL CH_4/g VS_{fed}) 426.7 ± 2.1 (PHB), 437.2 ± 8.3 (PHBV), 397.0 ± 15.6 (PHBH), 361.0 ± 1.8 (PLA), and 386.8 ± 6.4 (PLA/PCL). The ratio between the methane yield (BMP_{EXP}) experimentally recorded for pretreated and unpretreated bioplastics at the end of the experiment and its corresponding theoretical methane yield (BMP_{Th}) averaged 72.9 vs 73.9%, 74.5 vs 76.0%, 67.5 vs 77.6%, 77.4 vs 0.7%, and 74.3 vs 1.4% for PHB, PHBV, PHBH, PLA, and PLA/PCL, respectively (Fig. 2f). It is well recognized that the solubilization of bioplastics is a prerequisite for their efficient methanization and that mesophilic AD is commonly able to manage efficient hydrolysis of PHBs but not of PLA, due to the recalcitrant nature of the latter (Bernat et al., 2021; Cazaudehore et al., 2022a; García-Depraect et al., 2022a). This can explain the differences observed in mesophilic methane production for unpretreated PLA- and PHB-based materials. It should be also stressed that no accumulation of VFA in the final digestate was observed regardless of the experimental condition tested, and the final pH values were in the range of 6.6 to 6.9, indicating that all of the BMP tests performed well.

One of the main findings herein obtained is that alkaline pretreatment exerted a significant (p-value ≤ 0.05) enhancement of the methanization rate. Particularly, the *Rmax* estimated for PHB, PHBV and

PHBH increased from 10.6, 9.5 and 15.3 NmL CH_4/L-day to 59.5, 86.2 and 42.5 NmL CH_4/L-day, respectively, corresponding to a 5.6-, 9.1- and 2.7-fold improvement (Table 2). The acceleration in bioplastic methanization can be explained by the fact that the bioplastics subjected to alkaline pretreatment were most likely hydrolysed (to a significant extent) to monomers and/or oligomers that are, after a lag phase, rapidly and fully converted by the anaerobic microbial consortium/ metabolism. For instance, according to Myung et al. (2014), the thermo-alkaline hydrolysis of PHBV can theoretically lead to 3-hydroxybutyrate (3HB), crotonate, 3-hydroxyvalerate (3HV), 2-pentenoate, and 3-pentenoate, but experimentally the authors found 3HB and crotonate as the dominant products while the others were only detected at trace levels. In contrast, unpretreated bioplastics needed to be microbiologically depolymerized before any production of biogas occurs. PLA-based materials sustained maximum methanization rates of 14.8 and 16.5 NmL CH_4/L-day for PLA and the PLA/PCL composite, respectively. However, as mentioned above, unpretreated PLA-based materials failed to biodegrade under the experimental conditions and time scale tested in this study.

As stressed above, hydrolysis is the rate-limiting step of the overall AD of biodegradable bioplastics (Bátori et al., 2018; Cazaudehore et al., 2023; García-Depraect et al., 2022a; Narancic et al., 2018; Shrestha et al., 2020). It can be estimated, based on the maximum rates of methanization obtained, that 6–16 days of incubation in the case of pretreated PHBs and ~ 25 days for pretreated PLA-based bioplastics will be required to achieve 80% conversion to CH_4. In contrast, such a typical PHBs-to-CH_4 bioconversion will only occur after a longer retention time of 31–50 days without pretreatment. It has been recently reported that PLA-based materials need hundreds of days to be efficiently degraded under mesophilic AD conditions (Bernat et al., 2021; Cazaudehore et al., 2023). Overall, the findings herein presented and discussed support that applying proper alkaline pretreatment to the biodegradable bioplastics tested can allow for efficient methanization within the HRTs (30 days) commonly implemented by anaerobic digesters treating municipal organic waste. However, further studies are still needed to move this bioplastic valorization platform to full scale. For instance, the systematic assessment of the anaerobic biodegradability of pretreated and unpretreated manufactured products (e.g., packaging) under continuous co-digestion with food waste should be conducted before AD can be considered as an efficient and practical EOL option for biodegradable bioplastics.

3.3. Effect of alkaline pretreatment on anaerobic biodegradability and carbon fate

The final biodegradability values estimated for all pretreated and unpretreated bioplastics ranged between 81 and 86%, which agreed with that of the positive control (cellulose), except for the unpretreated PLA-made polymers, which remained non-biodegradable (Table 3). No significant differences (at p-value ≤ 0.05) between the final biodegradability of pretreated and unpretreated PHBs were observed. The biodegradability data herein recorded (on a gaseous carbon and DIC basis) are in good agreement with those previously reported for PHB (83.9%) and PHBV (81.2%), obtained after 77 days of incubation under mesophilic anaerobic aqueous conditions following the standard ISO 14853 (García-Depraect et al., 2022a). Similarly, Morse et al. (2011) reported that PHBH (3.8 mol% 3HH) films (0.3 mm thickness) lost 28% of their initial weight and near 100% after 7 and 12 days, respectively, of AD at 37 °C.

A carbon distribution analysis was performed to elucidate the fate of bioplastic carbon during AD. The share of residual carbon polymer (if any) was not determined and carbon sink due to biomass growth was assumed to be 10% (Chernicharo, 2007). In general, pretreated materials showed high carbon recoveries, on average between 94 and 98% (Table 3). However, alkaline pretreatment did not yield significantly (p-value ≤ 0.05) higher carbon recoveries, except in the case of PLA-based

Table 3

Final anaerobic biodegradability and carbon-flow distribution analysis for the different materials tested.

Material	BD, %[1]	Carbon as CH$_4$, %[2]	Carbon as CO$_2$, %[2]	DIC, %[2]	Dissolved TOC, %[2]	Total recovery, %[3]
Pretreated PHB	a 80.8 ± 0.4	a 50.2 ± 0.3	a 12.5 ± 0.3	a 18.2 ± 0.8	a 3.7 ± 0.2	a 94.5 ± 0.5
Unpretreated PHB	a 81.4 ± 2.2	a 50.9 ± 0.8	b 19.9 ± 0.2	b 10.6 ± 1.3	a 2.6 ± 0.7	a 94.0 ± 2.4
Pretreated PHBH[4]	a 81.6 ± 2.8	a 50.9 ± 3.6	a 12.7 ± 0.9	a 18.0 ± 1.7	a 4.6 ± 0.7	a 96.1 ± 3.5
Unpretreated PHBH	a 85.9 ± 2.5	a 54.1 ± 0.6	b 21.2 ± 0.8	b 10.6 ± 1.3	a 2.6 ± 0.7	a 98.5 ± 2.5
Pretreated PHBV	a 80.6 ± 3.5	a 51.3 ± 1.0	a 12.5 ± 1.7	a 16.8 ± 1.5	a 3.3 ± 0.5	a 93.9 ± 3.9
Unpretreated PHBV	a 80.9 ± 2.9	a 51.0 ± 1.8	b 20.5 ± 0.6	b 9.3 ± 3.0	b 1.8 ± 0.6	a 92.8 ± 3.5
Pretreated PLA	a 82.9 ± 1.2	a 47.4 ± 0.2	a 13.5 ± 0.0	a 22.1 ± 1.1	a 3.5 ± 0.1	a 96.4 ± 0.9
Unpretreated PLA	b 0.7 ± 0.6	b 0.4 ± 0.4	b 0.0 ± 0.0	b 0.2 ± 0.2	b 0.6 ± 0.9	b 1.3 ± 1.5
Pretreated PLA/PCL	a 84.4 ± 3.3	a 48.2 ± 0.8	a 12.9 ± 0.1	a 23.2 ± 2.5	a 3.6 ± 1.0	a 98.0 ± 4.1
Unpretreated PLA/PCL	b 1.3 ± 0.5	b 0.9 ± 0.1	b 0.1 ± 0.1	b 0.3 ± 0.5	b 0.6 ± 1.1	b 1.9 ± 1.6
Cellulose	82.3 ± 4.7	46.7 ± 1.8	23.7 ± 0.8	11.9 ± 2.1	1.8 ± 0.7	94.0 ± 5.1

[1] Biodegradability (BD) calculated as the sum of net gaseous carbon and net dissolved inorganic carbon divided by the initial carbon of the target material.
[2] Percentage calculated in relation to the initial amount of carbon present in the polymer.
[3] Biomass was assumed to be 10% of the total carbon contained in the polymer (Chernicharo, 2007).
[4] Data reported from duplicate tests as one outlier was removed. The initial amount of carbon present in each polymer was calculated based on its chemical structure.
A statistical comparison (one-way ANOVA) between the unpretreated and pretreated conditions was performed by type of bioplastic; for a specific bioplastic, same letter within a column indicates that values are not significantly different at *p*-value ≤ 0.05.

polymers, than those observed in tests carried out with untreated bioplastics. The total carbon recovery for the pretreated PLA/PCL blend and PLA was 98.0 ± 4.1 and 96.4 ± 0.9, respectively (Table 3). Most of the carbon originally present in the resin bioplastic was transformed into gaseous products, ~62.4% for pretreated PHBs and PLA-based materials and 72.0% for unpretreated PHBs and cellulose (Table 3). Importantly, while the C-CH$_4$ share did not differ significantly among all materials tested, the gaseous C-CO$_2$ share did decrease considerably to almost half of that compared to unpretreated bioplastic digestion. The DIC contents of pretreated bioplastics were significantly increased due to the sodium carbonate-bicarbonate equilibrium. Indeed, the final pH values of the digestates were on average 6.6 and 6.9 for untreated and pretreated bioplastics, respectively (data not shown). Dissolved organic carbon accounted for approximately 3% of the initial carbon present in the materials regardless of whether they were pretreated or not, except in the case of unpretreated PHBV, which showed a slightly lower dissolved TOC content of 1.8% but quite similar to that of cellulose tests (Table 3). Interestingly, the dissolved TOC was not associated (even partially) to VFAs, as such degradation intermediate products of the AD process did not accumulate at all at the end of the experiment. More in-depth analyses for the detection and quantification of organics, including residual (micro)plastics, are needed in future investigations.

4. Conclusions

The impact of alkaline pretreatment on the carbon solubilization efficiency of PHB, PHBV PHBH, PLA and a PLA/PCL blend was investigated. The efficiency at which bioplastics were alkali hydrolysed mainly depended on the physical–chemical structure and concentration of the bioplastic, NaOH concentration and reaction time. Overall, compared to PHB and associated co-polymers, PLA-based materials showed a different response to the alkaline pretreatment. Particularly, PLA and the PLA/PCL blend were more easily decomposed than most PHB-based materials (92–98% *vs.* 80–93% carbon solubilization). BMP tests devoted to assessing the impact of alkaline pretreatment on the yields and kinetics of biogas production were also performed and evidenced that the methanization rate of all bioplastics tested can be substantially enhanced by alkaline pretreatment. No lag phases were observed with pretreated PLA-based materials while pretreated PHB-based materials required extended adaptation times, stressing the difference existing between PLA- and PHB-based materials. The methane production potential data recorded for pretreated and untreated PHB-based bioplastics did not differ significantly, except in the case of pretreated PHBH, which reached a methane yield 14% lower than its control. Alkaline pretreatment enabled PLA and PLA/PCL to be anaerobically digested, whereas their unpretreated counterparts failed

to biodegrade under the experimental conditions and timeframe tested. The carbon mass balance conducted revealed that biogas was the major carbon sink followed by DIC, the latter was comparatively higher when pretreating the materials. Last but not least, the final share of dissolved organic carbon remained below 5% regardless of the bioplastic type and was not explained by the presence/accumulation of VFAs in the digestate, pointing out the need for further analytical detection and quantification of organic compounds.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: O.G.-D., L.J.M.-M.,S.R.-V.,R.L.,R.A.B.,T.B.,R.M. reports financial support was provided by Société des Produits Nestlé S.A. R.A.B. reports a relationship with Société des Produits Nestlé S.A. that includes: employment. T.B. was employed by Société des Produits Nestlé S.A. during the development of this research.

Data availability

Data will be made available on request.

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