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VALORISATION OF EYEWEAR BIOPLASTICS THROUGH HTC AND ANAEROBIC DIGESTION: PRELIMINARY RESULTS

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ABSTRACT

Bioplastics are increasingly replacing traditional plastics in many sectors, but the legislative and operative frameworks for their disposal remain unclear: they should be collected and treated together with the organic fraction of municipal solid waste (OFMSW), but often do not biodegrade satisfactorily in the plants that treat OFMSW. This work focuses on a type of cellulose diacetate employed in the eyewear industry to analyse hydrothermal carbonization (HTC) as a pre-treatment before anaerobic digestion (AD). The results show that HTC can hydrolyse this bioplastic even at moderate temperatures, reaching an almost total dissolution in the liquid phase at 210°C and, at higher temperatures, producing hydrochar. When the HTC slurry obtained at 210°C is fed to mesophilic or thermophilic AD, both the amount and the production rate of biogas are enhanced compared to the raw bioplastic. In particular, in thermophilic conditions, the amount of produced biogas undergoes at least a threefold increase compared to the untreated cellulose diacetate. Thus, this work confirms that a prior HTC step may be a suitable approach to enhance the disposal and energy recovery of bioplastics through AD.

1. INTRODUCTION

Bio-based plastics (or simply "bioplastics") is an umbrella term that identifies materials that are similar to traditional plastics in their mechanical properties, but are either biodegradable or obtained from biomass (or, in most cases, both) (Karan et al., 2019; Nandakumar et al., 2021; RameshKumar et al., 2020; Thakur et al., 2018). The depletion of fossil sources and the environmental impact of traditional plastics have fostered the development of bioplastics, which are slowly but steadily growing in many applications. Nonetheless, for bioplastics to become completely established, more research is needed in order to clarify some still controversial aspects.

Most commercial bioplastics are labelled as biodegradable or compostable. "Biodegradable" merely describes a material that can be broken down due to the action of microorganisms; conversely, "compostable" specifies that a biodegradable material can disintegrate into non-toxic substances in composting conditions and within a specific time frame. In principle, compostable bioplastics should be collected with the organic fraction of municipal solid waste (OFMSW) and disposed of through the same methodologies. However, the tests to assess whether a material can be defined as compostable (mainly based on UNI EN 13432 and UNI EN 14995) employ harsher conditions and longer residence times than those of most plants that treat the OFMSW – often through a sequence of anaerobic digestion and composting. As a result, in real plants bioplastics often do not biodegrade satisfactorily (Folino et al., 2023), slowing down or clogging the whole process or reducing the quality of the produced compost (Gadaleta et al., 2023). Several news outlets have reported on cases from Italian OFMSW treatment plants in which bioplastics are discarded at the entrance of plants and sent to landfilling (Athanassiou, 2021; il Dolomiti, 2019; Il Tirreno Empoli, 2019), which is a deprecated and inefficient way to dispose of organic waste. The scientific community is also increasingly aware of the problem. Battista et al. (2021) experimentally proved that most bioplastics have a low biogas production and long biodegradation time, which are not enhanced by chemical pretreatments via acids or bases at room temperature. Cazaudehore et al. (2023) showed that polyhydroxybutyrate (PHB) can be biodegraded together with biowaste, while for polylactic acid (PLA) a previous thermo-alkaline pre-treatment was necessary. The recent review by Vardar et al. (2022) further emphasises that the biodegradability of bioplastics in anaerobic digestion sys-

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tems is often unsatisfactory, and that pre- and post-treatment methodologies must be further investigated to make these materials treatable by OFMSW plants.

The hydrothermal carbonization (HTC) process may represent a solution to this problem. HTC is an induced coalification process, performed in a temperature range of 180–250°C and in liquid water. It is able to treat a wide variety of carbonaceous feedstocks, including MSW, breaking their heavy constituent molecules into simpler ones. The products are the hydrochar (solid fraction), the HTC liquor (liquid fraction) and gases (mainly CO_2). When the hydrochar and/or the HTC liquor are fed to anaerobic digestion or composting facilities, they enhance the performance of the plants, increasing the product yield and quality (Ischia & Fiori, 2021), as assessed by a few recent studies (Bona et al., 2022; Ferrentino et al., 2020; González et al., 2021; Scrinzi et al., 2022). HTC has been applied to various types of biomass and waste, and hydrothermal processes were also proved suitable to decompose traditional plastics, despite sometimes requiring harsh operative conditions or the use of a catalyst (Mumtaz et al., 2023). However, researchers have neither reported whether the HTC of bioplastics is feasible nor if it can facilitate anaerobic digestion. This study aims at investigating this research gap, assessing whether a prior HTC step can enhance the disposal of residual eyewear bioplastics by promoting their conversion into valuable products, such as biogas and biomethane.

This work is part of the Occhio al Bio! project (literally "watch out for the bio!"), funded by Fondazione Cariverona and involving the University of Trento and Certottica. The project is aimed at tackling the uncertainty in the labelling and policy framework, and the correct and most fruitful approach to dispose of bioplastics, focusing on those employed in eyewear production (frames, lenses, etc.). Eyewear is a very large industry: it is estimated that 1.2 billion people use glasses, which are almost always made of plastic materials. The share of bioplastics in eyewear is increasing, but there is a complete lack of a policy framework to certify that a specific product is truly bio-based and to describe how the residual material should be disposed of. Although at present polylactic acid (PLA) is the most abundantly produced bioplastic, in the eyewear industry cellulose acetates constitute by far the main class of employed bioplastics. One of the typical applications of cellulose acetate (in particular cellulose diacetate, CDA) is in the eyewear sector, especially for the manufacture of spectacle frames (Gilbert, 2017; Hansraj et al., 2021), due to its sensorial and hypoallergenic characteristics (Carollo & Grospietro, 2004; Hansraj et al., 2021) and eco-friendliness (Kabasci, 2020). By contacting eyewear companies, we were able to confirm that CDA is by far the most employed bioplastic in the eyewear industry, although no official data on its market share are available. Contextually, in the last years, companies are moving towards formulations with biobased plasticisers, avoiding the use of diethyl phthalate.

In this framework, the present work employed CDA as a case study with the aim of verifying whether a combination of HTC and anaerobic digestion can be a valid route to enhance the disposal phase.

2. MATERIALS AND METHODS

2.1 Employed bioplastic

The chosen bioplastic feedstock (in the following referred to as CDA) is commercially known as M49. It is based on cellulose diacetate, and was provided in the form of 2x2x1 cm blocks, with an average mass of about 3.5 g per block. Despite not being as commercially widespread as other types of bioplastics, cellulose acetates are widely employed for various applications, such as membranes, cigarette filters, photographic films and packaging. Puls et al. (2011) estimated its global production to be about 800 kton/y in 2008, and unverifiable web searches suggest that this amount may have undergone a tenfold increase in recent years. The literature on the biodegradation of cellulose acetate materials is often contradictory (Puls et al., 2011; Yadav & Hakkarainen, 2021), and the biodegradability of the material depends on several factors, such as the degree of acetylation, the presence of additives, and the biodegradation environment. Kosheleva et al. (2023) reported that cellulose acetate can be biodegraded via anaerobic digestion, but at significantly lower rates than food waste, which further decrease when the test is performed in a semi-continuous apparatus rather than in a batch one. To the best of the authors' knowledge, the literature does not feature any article reporting on the HTC of cellulose acetate.

CDA was characterised in terms of elemental composition through a LECO 628 Elemental Analyser in accordance with ASTM D-5375 for carbon, hydrogen and nitrogen. The ash content was determined by keeping a sample of CDA at 550°C overnight. The oxygen content was determined by difference with the percentages of C, H, N, and ash. Table 1 reports its composition.

2.2 HTC tests

The HTC runs were performed in a 50 mL batch reactor built in-house at the University of Trento, described in detail in previous publications (Fiori et al., 2014). Each test was performed at least twice. At the beginning of each HTC run, a CDA block was placed inside the reactor together with tap water, at a fixed bioplastic to water mass ratio of 0.125. Then, the reactor was closed, flushed with nitrogen, and heated through an electric resistance up to the selected temperature (180,190, 200, 210, 220 and 250°C). The residence or reaction time was counted after the reactor had reached the set point temperature; the heating time from room temperature to set point temperature was approximately 15-20 minutes. After a residence time of 1 h, the reactor was quickly cooled down dipping it in liquid water. The produced gas volume was measured by letting it flow in a closed water column and measuring the displacement of the water head. Then, the reactor was opened, and its content was filtered with a 0.45 µm filter, separating the

TABLE 1: Elemental composition of CDA (mass fractions, with O calculated by difference).

C (%)	H (%)	N (%)	O (%)	Ash (%)
48.9 ± 0.1	6.2 ± 0.3	0.0	44.9 ± 0.3	0.0

HTC liquor from the hydrochar, which was dried at 105°C overnight – also the HTC reactor was placed in the oven at 105°C overnight. After the drying phase, the reactor and the filter were weighted to assess the mass of the produced hydrochar.

The solid yield (SY) was calculated as the ratio between the mass of the hydrochar produced and that of the initial bioplastic block. The mass of the gas produced was calculated through the ideal gas law, assuming the gas entirely consisted of CO_2; from this, the gas yield (GY) was calculated by dividing the mass of the gas produced by the initial mass of the bioplastic. Finally, the liquid yield (LY) was calculated as the one's complement of SY and GY. The yields are reported in percentage terms in what follows.

2.3 Anaerobic digestion tests

The anaerobic digestion tests were performed on the untreated bioplastic and on the whole slurry resulting from the HTC process (i.e. the mixture of liquid and solid products), selecting the temperature for which the highest liquid yield was achieved. The slurry was characterised by chemical analyses performed in triplicate. Volatile solids (VS), total solids (TS), total chemical oxygen demand (TCOD), soluble COD (sCOD) were quantified according to Standard Methods (APHA et al., 2012). sCOD was measured after sample filtration on a 0.45 µm paper filter. Total organic carbon (TOC) was measured using a TOC/TN analyzer (Formacs^{HT-I}, Skalar).

Biochemical methane potential (BMP) tests were carried out to assess the anaerobic biodegradability of the untreated bioplastic and the whole HTC slurry produced from CDA. Tests were conducted in both mesophilic and thermophilic conditions using serum bottles of 135 mL volume inoculated with anaerobically digested sludge. For mesophilic conditions, digestate samples from the Trento (Trentino, Italy) wastewater treatment plant (M-WW) and Lana (South Tyrol, Italy) OFMSW treatment plant (M-OF) were used as inoculum. Moreover, a digestate sample from the Cadino (Trentino, Italy) OFMSW treatment plant (T-OF) was used as the inoculum for thermophilic tests after its dilution with tap water to obtain a TS content approximately equal to 3%. The use of three different inoculums was chosen to operate with three different bacterial communities and evaluate their influence on the variation in specific biogas production. The main characteristics of the three inoculums used are reported in Table 2.

The inoculums were pre-incubated for 14 days at 37 ± 0.1°C and 55 ± 0.1°C, respectively, for the mesophilic and thermophilic conditions to completely biodegrade the organic substances eventually present in the digestate used as inoculum. The anaerobic digestion tests were carried out in duplicate considering a feeding/inoculum ratio (F/I) equal to 0.5 g $VS_{substrate}$/g $VS_{inoculum}$, with a serum bottle volume fixed at 80 mL. Biogas and biomethane productions were measured according to the procedure reported by Ferrentino et al. (2019). The BMP tests were continuously monitored and stopped when no further changes in the biogas production were observed. Data collected allowed the determination of the daily biogas production (DBP), expressed as mL_{biogas}/d, while cumulative data allowed the evaluation of the specific biogas production (SBP), reported as mL_{biogas}/g VS_{added}. Moreover, the percentage of biodegraded organic matter converted into methane was evaluated according to the method proposed by Beniche et al. (2021).

3. RESULTS AND DISCUSSION

3.1 HTC

The results of the tests show that HTC is effective for decomposing CDA; Figure 1 shows the trends of the product yields against temperature. In all cases, the solid yield is lower than 100%, proving that even at the lowest temperatures the material undergoes a sort of solubilisation. There is a sharp change between 190 and 200°C, as proved by the drastic decrease of the solid yield: such a small temperature variation is evidently sufficient to activate decomposition reactions, causing nearly all the bioplastic constituents to dissolve into the liquid phase. The solid yield reaches a minimum at 210°C (7.2%) and increases again for higher temperatures, achieving a maximum value of 20.4% at 250°C. This is probably due to the formation of secondary char through the back polymerisation and condensation of organics dissolved into the liquid phase. Meanwhile, the liquid yield follows a trend opposite to that of the solid, while the gas yield increases with the temperature due to a higher occurrence of carboxylation and decarbonylation reactions.

Figure 2 shows the appearance of CDA and of the solid products of HTC, obtained at different temperatures. From

TABLE 2: Properties of the inoculums.

	M-WW	M-OF	T-OF
TS [%]	2.9 ± 0.1	3.8 ± 0.1	3.0 ± 0.2
VS [%]	72.5 ± 1.1	56.7 ± 1.3	60.8 ± 0.6
TKN [mg TKN/L]	2300 ± 100	4400 ± 250	1800 ± 90
NH_4-N [mg NH4-N/L]	1110 ± 30	3030 ± 110	1200 ± 20
PO_4-P [mg PO4-P/L]	121 ± 5	129 ± 8	230 ± 10
TP [mg TP/L]	860 ± 30	570 ± 40	260 ± 5
sCOD [mg sCOD/L]	1500 ± 400	6050 ± 450	4800 ± 230
COD [mg COD/L]	22100 ± 3500	27100 ± 2250	23400 ± 3600
pH	7.6 ± 0.5	7.9 ± 0.4	7.3 ± 0.2

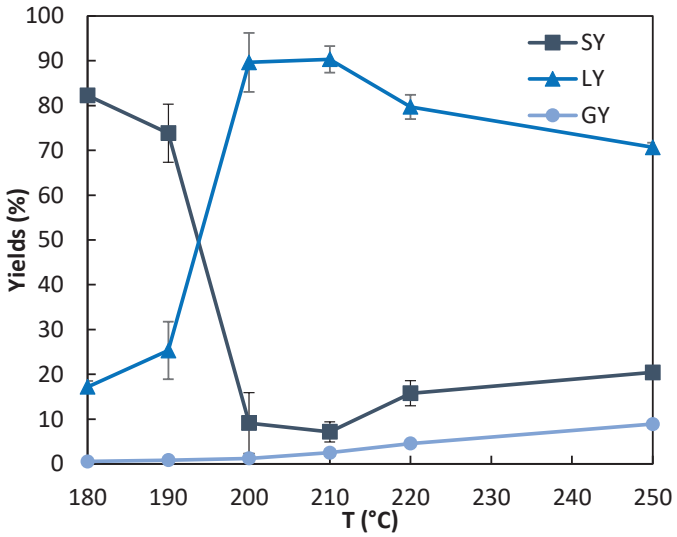

FIGURE 1: Trend of the solid (SY), liquid (LY) and gas (GY) yields for the HTC of CDA at various temperatures. The indicators represent the experimental data, the curves connecting the indicators are intended to help the reader in the comprehension of the figure.

FIGURE 2: Appearance of CDA and of the solid products obtained at different HTC temperatures.

a visual point of view, when treated at 180 and 190°C the material becomes white and still appears plastic-like. Given the high values of the solid yield, it is likely that only some additives are released, but the CDA core structure is not significantly altered. As temperature increases, the solid products are more visibly altered and, at the highest value of 250°C, they show the typical appearance of hydrochar, being black and granular.

Figure 3 displays the trend of the pH of the HTC liquor against temperature. The pH markedly decreases in the 180-210°C temperature range, whereas it seems to be mostly constant in the 210-250°C range. The pH decrease indicates the increasing concentration of acids in the liquid phase; these may be both compounds that are released from the polymer (such as acetic acid) and other acids that form due to the HTC reactions (Ischia et al., 2022). The relatively low value of the pH at 180°C further proves that the material undergoes some sort of solubilisation even at the lowest tested temperature, despite its change in appearance is not as drastic as for the other temperatures.

From a chemical point of view, the behaviour observed for CDA is rather unusual and not comparable to that of other feedstocks under HTC conditions. For example, the solid yield of plain cellulose diminishes monotonically with increasing values of the HTC temperature (Volpe et al., 2020). While it is difficult to explain this behaviour without detailed chemical analyses, it is known that for cellulose acetate the action of heat causes the release of acetyl groups from the cellulose backbone, which represents the first step in its decomposition (Yadav & Hakkarainen, 2021). This causes the formation of acetic acid, known to catalyse the HTC reactions (Lynam et al., 2011). Thus, the cellulose backbone undergoes chain scissions, leading to the formation of sugar derivatives (like furfural and 5-HMF) and other decomposition compounds dissolved into the liquid phase. At higher temperatures, these compounds undergo repolymerisation and condensation reactions, forming the abovementioned secondary char (Ischia et al., 2022). The trend of the pH seems to support these observations.

On the one hand, the HTC operative conditions that originate the highest liquid yield may be the most suitable for a subsequent anaerobic digestion step, due to the improved accessibility to microorganisms of the chemical species dissolved in the liquid phase. On the other hand, hydrochar is well known for having several interesting applications (Masoumi et al., 2021) – for example, it could simply be burned or gasified, providing thermal energy in a possible biorefinery, or be used as a base for advanced carbons, like adsorbents (Purnomo et al., 2018). While these applications are interesting and may be suitable to valorise a relatively pure stream of cellulose acetates, this

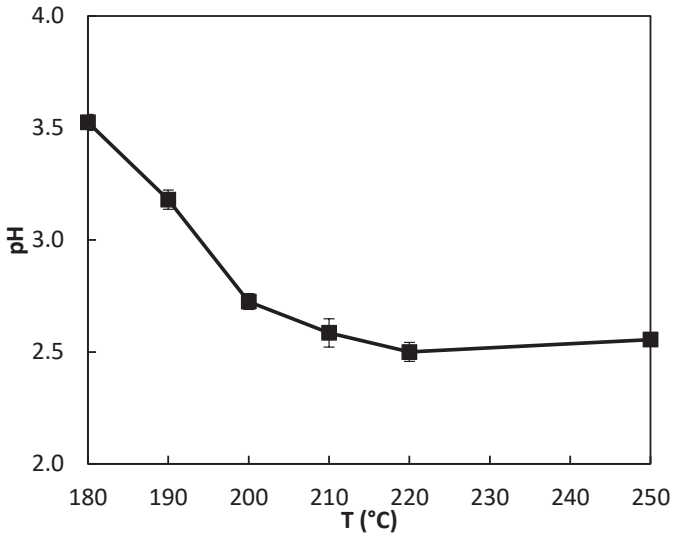

FIGURE 3: Trend of the pH of the HTC liquor at various temperatures. The indicators represent the experimental data, the curve connecting the indicators is intended to help the reader in the comprehension of the figure.

work strictly focuses on applying HTC as a pre-treatment to anaerobic digestion, with the aim of enhancing the already-existing disposal chain for OFMSW. Thus, extensive characterisations of the hydrochar and liquor as a function of the HTC operative conditions are left for future studies.

3.2 Anaerobic digestion

The anaerobic digestion tests were run on the untreated bioplastic and on the slurry (i.e. hydrochar plus HTC liquor, without any filtration) obtained from HTC at 210°C, which showed the highest liquid yield. The HTC slurry had the following characteristics: 5.3±0.1% TS, 99.5±0.1% VS, 120±5 g COD/L, 50±5 g TOC/L and pH equal to 2.3±0.5. At the beginning of the test, each sample of CDA or HTC slurry was mixed with the inoculum. The pH of the mixture of all the BMP tests ranged between 6.7 and 7.6.

Figure 4a depicts the cumulative SBP. Starting from the raw CDA, it is clear that anaerobic digestion is unable to biodegrade this material satisfactorily (or at all): the final production of biogas is null for the M-OF inoculum and low for the T-OF inoculum. This result agrees with some previous literature, in which thermophilic conditions were reported to be more efficient in biodegrading bioplastics (Yu et al., 2023). Since the inoculums used for the BMP tests were collected in plants where different criteria for OFMSW collection are used, it is likely that the microbial communities are different due to the adaptation to different feedstocks. In the municipalities served by the OFMSW plant in Lana, the disposal of bioplastics, even in the form of collection bags, into OFMSW is strictly prohibited. On the contrary, it has been estimated that the OFMSW sent to the Cadino plant has a mass fraction of bioplastics of about 4%. Since the addition of bioplastics to the OFMSW influences the microbial communities (Bandini et al., 2022), it is possible that with longer residence times and adaption the biodegradation of CDA might increase. However, this aspect needs to be deeply investigated in future works. Moreover, it should be pointed out that reducing the size of the CDA block (for instance by milling) may increase its biodegradability, despite being energy consuming. However, since this is unlikely to happen in a real OFMSW treatment plant and since the whole block was also fed to the HTC process, we decided to feed the whole block to anaerobic digestion as well.

Compared to raw CDA, HTC markedly increases the biogas production. Since HTC converts almost all the bioplastic to liquid compounds, the feedstock becomes much more accessible to microorganisms, as shown by the fact that the biogas production peak is reached after 1-2 days from the beginning of the BMP test (Figure 4b). For the T-OF inoculum, two separate peaks can be observed, which are likely ascribable to the biodegradation of different compounds. The trends of the biomethane production are not reported, as they are identical to those of biogas that are shown in Figure 4, with the methane/biogas volume ratio always ranging between 56% and 59%.

By employing the methodology by Beniche et al. (2021), we were able to assess that a complete biodegradation of the COD could not be achieved in any test. However, the biodegradability of the untreated CDA was 0% in mesophilic conditions and 4% in thermophilic conditions; a pre-treatment with HTC causes at least a threefold increase of this value, which respectively becomes 12%, 13% and 15% for M-OF, T-OF and M-WW. Although there are no studies in the literature on pre-treating CDA via HTC before anaerobic digestion, the results of this study can be compared with previous studies on anaerobic biodegradation of cellulose-based bioplastics. Yagi et al. (2009) achieved a total of 80% biodegradation of cellulose under mesophilic and thermophilic conditions in 15 and 13 days, respectively. Both Calabro' et al. (2020) and Shin et al. (1997) found significant methane production from cellulose-based bioplastics, namely 310 L CH_4/kg VS and a methane conversion efficiency of 85% in 44 and 20 days, respectively. On the contrary, Gomez and Michel Jr (2013) observed that after 50 days of anaerobic digestion, only 20-25% of the test-

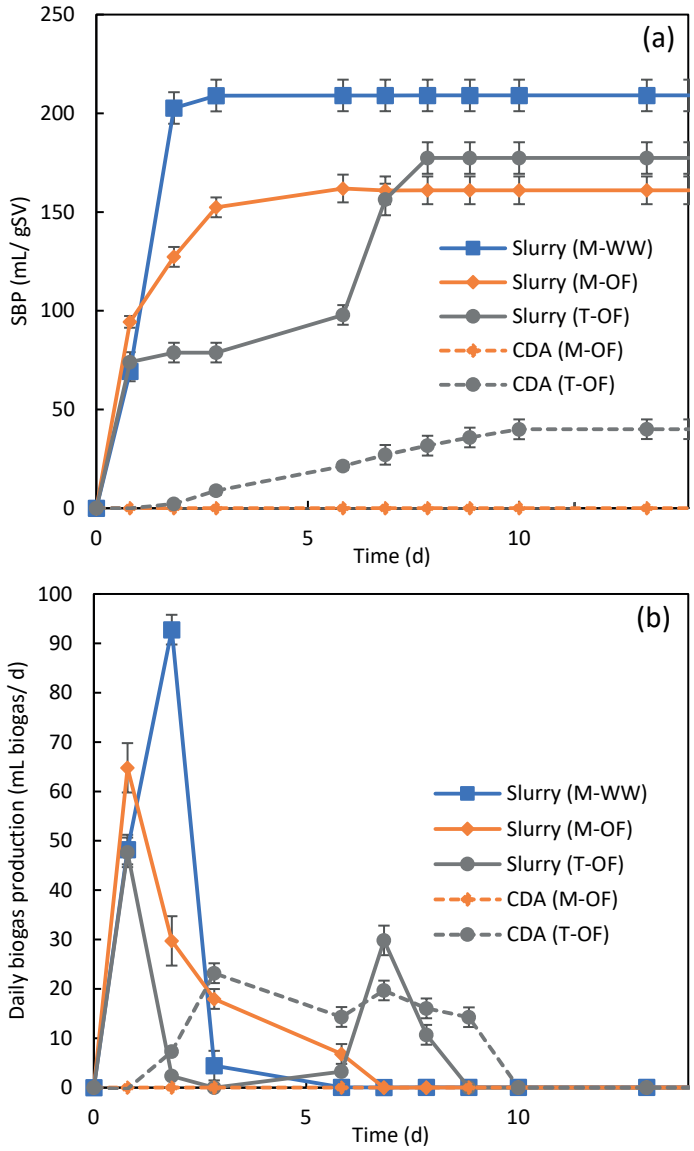

FIGURE 4: Cumulative (a) and daily (b) specific biogas production obtained in the BMP tests. The indicators represent the experimental data, the curves connecting the indicators are intended to help the reader in the comprehension of the figure.

ed bioplastics were converted into biogas. Furthermore, Puechner et al. (1995) observed a low degree of biodegradation for cellulose acetate, which was 22% in 60 days. It can thus be noted that the results of previous studies on anaerobic biodegradation of cellulose-based bioplastic are very different.

In any case, these results confirm that HTC is a valid pre-treatment for bioplastics that are destined to anaerobic digestion, both increasing the biogas production and shortening the biodegradation time.

4. CONCLUSIONS

A commercial bioplastic based on cellulose diacetate and employed in the eyewear industry was subjected to HTC at temperatures ranging from 180 to 250°C. The material reaches its highest solubilisation level at 210°C, with a residual solid yield of 7.2% and most of the bioplastic dissolved in the liquid phase. For the higher tested temperatures, the solid yield notably increases, likely due to the formation of secondary char due to liquid-to-solid reactions (e.g., polycondensation). The behaviour of cellulose diacetate under HTC conditions is interesting and will be analysed in greater detail in future works, in order to assess the decomposition pathway and products.

The anaerobic digestion (BMP) tests showed that this bioplastic as it is is poorly biodegraded by microbial activity, with low or null biogas yields depending on the employed inoculum. If the HTC slurry is fed to anaerobic digestion instead, both the biogas yield and the biodegradation rate are markedly enhanced, with the peak in the biogas production being reached within a couple of days from the beginning of the BMP test. Also in the case of anaerobic digestion, there are specific aspects that merit to be studied in better detail, such as the role and adaptability of the microbial communities.

In summary, coupling HTC and anaerobic digestion appears as a valuable and effective strategy to enhance biomethane production from waste bioplastics, at the same time facilitating their disposal. While this study focused on a selected bioplastic and batch anaerobic digestion tests, future works may explore whether the present conclusions are still valid when processing a mixture of bioplastics (or bioplastics and traditional plastics) and other organic residues, and how the microbial communities may adapt to these changes in the feedstock.

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