Anaerobic digestion of organic waste allows recovering energy and enhancing the subsequent bioplastic degradation in soil

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Abstract

The bioplastics within organic municipal waste are a critical component for the future of waste management with particular reference to the quality of the final products, i.e., digestate and compost. Moreover, to promote a circular economy they need to be recovered to produce new material and/or energy. This study compared polylactic acid (PLA) and starch based (SB) materials which were subjected to anaerobic digestion (AD) treatments producing biomethane, and the fate of residual bioplastics when incubated in soil were then evaluated. Results indicated that AD processes affected both PLA and SB characteristics, influencing their subsequent degradation in soil. Comparative material balance, considering the whole process, indicated that SB bioplastics degraded by 50%, while PLA achieved overall degradation by 70% when thermophilic AD was applied. The insights obtained contribute to understanding the fate of bioplastics and confirmed the role of AD as method for waste valorization in a circular economy perspective.

Keywords:

Anaerobic Digestion; Biodegradation in soil; Mass Balance; Residual processed bioplastics; Waste management.

Introduction

The organic waste management system for the separate collection and the recycling of the organic fraction of municipal solid waste (OFMSW) is currently regulated at the EU level by the Waste Framework Directive (2008/98/EC) and it mainly comprises biological treatments such as composting or integrated anaerobic-composting digestion (De Clercq et al., 2017; Martinez-Sanchez et al., 2016). These treatment technologies are well known strategies to recover energy and material, i.e. biomethane and renewable fertilizers (digestate/compost), connecting waste management to the circular economy policy, which aims to valorize urban biowaste (Pecorini et al., 2020).

However, and with particular attention to the use of the final products as fertilizers or soil amendments for agronomic purposes, there are various environmental concerns that must be considered before those waste-derived fertilizers can be used, avoiding the input to the soil of any contaminants such as organic and inorganic pollutants and/or inert materials such as plastics to the soil (Van Roijen and Miller, 2022; Liwarska-Bizukojc, 2021; Ruggero et al., 2019). To reduce this kind of pollution and plastic contamination of soils, a policy legislative framework and several measures such as the directive on single use plastics (EU 2019/904), as well as the standardized procedures and specified requirements (e.g. EN13432 and EN14995) for industrial compostable bioplastic, were recently proposed by the European Commission.

Such regulations are not only promoting the marketing of biodegradable bioplastics from renewable biomass as sustainable replacements for petroleum-based plastics, but also encourage the development of an efficient system for the correct separate collection, treatment, and end of life routes of such biomaterials (Huerta-Lwanga et al., 2021).

One of the key issues in this context is related to the integration of biodegradable bioplastics in the biowaste management chain and so in the composting and anaerobic digestion (AD)

facilities, which in the near future, will have to deal with the increase and the impact of these organic fraction materials within the OFMSW (Abraham et al., 2021; Cucina et al., 2021). Organic waste separately collected in Italy, one of the major OFMSW producers in Europe, resulted in about 6.4 Mg in 2019 and is expected to grow by 50% by 2025 with respect to current levels, with a significant upgrading of composting facilities to incorporate AD (ISPRA, 2020; Bruni et al., 2020; Cucchiella et al., 2019).

The collection of bioplastics within the OFMSW and their recovery through organic waste biological treatment systems with a view to efficient management of their end-of-life strategies, will increase with levels of bioplastics in wastes, possibly reaching concentrations of 8 –10% (on a weight basis) of OFMSW (Cucina et al., 2021b). However, some of these bioplastics cannot be completely biodegraded during waste treatment because the conditions which occur during the process are different from those adopted for standardized methods used to achieve biodegradability. Sometimes biological approaches do not reach the target of getting complete degradation of bioplastics during waste management (Mohee et al., 2008; Ruggero et al., 2019). The consequence of that is an incomplete biodegradation of some polymers, which can negatively affect the efficiency of bio-waste management in terms of both energy production (biomethane production in AD) and final products' quality, i.e., it may result in a high content of plastic (bioplastics) in digestate and compost (Calabro' et al., 2020).

In this context, many studies have sought to understand the biodegradation of bioplastics and have identified methodologies to monitor the biodegradation levels during waste treatment (Cucina et al., 2022a). Recently, Cucina et al., (2021a) reviewed literature on the fate of bioplastics through the waste management process and strategies to improve degradation kinetics of bioplastics in different environments. The Authors highlighted the need for further research to fill the knowledge gap in the controversial degradation kinetic results which

79 derive from the complexity of biopolymers, composites and blends that constitute bioplastics.
80 As well as this, there was much variability in the experimental conditions adopted during the
81 actual waste management processes, compared to those adopted for testing bioplastic
82 degradation in aerobic and anaerobic conditions. In a previous work (Cucina et al., 2021b),
83 decomposition of two different biobased and compostable plastics blends was tested through
84 biological treatments such as AD and subsequent composting of the digestate. This included
85 evaluating the impact of such bioplastics, loaded at a high dose into the systems, in view of
86 what could happen by 2030, when an increase in the amount of bioplastics in the OFMSW is
87 expected. The AD of organic waste is a commercial process that has already been
88 extensively investigated and has been recognized as good way to recover organic energy.
89 The OFMSW produces large amounts of biomethane that was reported to be in the range 300
90 and 600 NL kg^{-1} VS (Campuzano and González-Martínez, 2016; Alibardi et al., 2015). In
91 addition, residual waste from AD, i.e. digestate, can be usefully recovered as fertilizers to be
92 used in substitution of synthetic mineral fertilizers. Bioplastics are expected to contribute
93 largely to the organic fraction of municipal solid (OFMSW) waste. Cucina et al., (2022b)
94 indicated that bioplastics could represent about 7–8 % by weight of OFMSW in Italy by
95 2030, posing new questions about their fate during waste management (bioplastic
96 degradability) and in residual waste (digestate and compost quality). However, the increase in
97 OFMSW of bioplastics capable of being biologically degradable, could, ultimately lead to
98 substantial increases in biogas production (Cucina et al., 2022b). Therefore, potential
99 degradability of bioplastics in AD has become an important issue in terms of biomethane
100 production by OFMSW while also affecting digestate quality, i.e. residual bioplastic presence
101 in biofertilizers and soil.
102 Our study suggested the need to enhance the rate and amount of bioplastic degradation during
103 the waste management process, which could play a key role in reducing the amount of

bioplastics that eventually reach the soil. In general, the majority of the studies performed on the most promising and widespread bioplastics, such as those made of polylactic acid (PLA) blends, have demonstrated a significant biodegradation under AD in case studies under thermophilic conditions, during which biodegradation is promoted by the temperature, leading to a lower impact on the quality of the digestate (Calabro' et al., 2020; Folino et al., 2020).

The key role played by temperature during AD has also been reported for compostable shoppers largely made of starch which showed shorter degradation times under thermophilic conditions than in mesophilic tests (148 ± 92 days vs. 376 ± 319 days respectively) (Calabro' et al., 2020; Cazaudehore et al., 2021).

Chemically, PLA is a linear aliphatic polyester obtained from polymerization of lactic acid produced by bacteria during the fermentation of starch and sugars from renewable crops (*e.g.* sugar beet, sugar cane or corn) and its uses typically include disposable items such as cutlery, drinking vessels, dishes and packaging. The starch-based bioplastic of which most of the bioplastic bags used for organic waste are made, represented about 20% of the bioplastics produced in 2020. Starch-based blends are composed mainly of polybutylene adipate terephthalate, 10% of additives, and starch, one of the most abundant and renewable polysaccharides, obtained from plants (e.g. corn, rice, potato). Starch consists of amylose and amylopectin, two types of glucose polymers whose units are connected by α-1,-4 bonds or α-1,-6 bonds respectively.

High bioplastic contents in digestate/compost raises some questions that go beyond the qualitative aspect of the final products, and are related to biodegradation of these biopolymers' residues in soils (De Girolamo et al., 2019); if from a qualitative point of view of the final products (compost and digestate) they are still officially classified as "plastic", in reality they are bioplastic and so formally, completely biodegradable in soil.

In recent decades investigation into the degradation of bioplastics in the soil is arousing interest in the scientific community, with reports showing for such biopolymers (e.g. PLA and starch blends), regardless of conditions tested, significantly faster degradation rates than the time required by petroleum-based plastics which severely accumulate in soil environments (Chamas et al., 2020). For instance, several studies have shown the importance of intrinsic biodegradability in reducing bioplastics' residual life and their persistence in soil environments (Degli Innocenti and Breton, 2020). Cucina et al., (2021) in a comparison study on biodegradation kinetics constants, reviewed the estimated times for complete degradation in soil, indicating half-life times with complete degradation in soil achieved in 591 ± 313 and 1,604 ± 1,010 days for starch-based and PLA bioplastics, respectively.

Despite the active investigations focused on elucidating the behavior of biodegradable bioplastics in AD and composting processing under the current industrial management systems and with different operating conditions, there is still much to understand, especially towards assessing the overall fate, the degree of degradation and the impact of applying such digested polymeric organic fragments to the soil. No information is yet available in the literature regarding the effect of waste management of bioplastics on the subsequent degradability in soil.

Furthermore, only limited information is available in the literature on the role of the application of solid digestate to the soil, with most reports relating to the benefits of its application on microbial activities, plant growth and soil fertility (Holatko et al., 2021; Anae et al., 2021), but not on its effect on the presence of any residual biopolymers nor on its possible improvements as an organic amendment when incorporated in the soil.

This work aims to provide insights about the degradation in soil of two residual processed bioplastics, elucidating their degradation mechanisms as a function of different treatments and polymer mixtures. We compared PLA and SB materials after they were subjected to

mesophilic or thermophilic AD and composting treatments, to identify and assess the effect of the different conditions adopted during waste management on the bioplastics properties by measuring degradation rates and kinetics in soil. We also included the addition of a digestate in comparison with soil alone, so as to explore whether it could favor degradability of the residual bioplastics tested by providing a medium with stable carbon, extra nutrients and bacteria for treating organic waste containing bioplastics.

Material and Methods

2.1 Bioplastic samples

Two types of bioplastic materials were used in this work: a commercially available starch-based blend (SB) and a mixture of PLA (P) cutlery bioplastics, both compostable according to standard (EN13432, 2002) and labeled by the Italian Composting Association (CIC) (Italy) and TÜV Austria (Austria). Bioplastics, i.e., PLA and starch-based, underwent various biological processes under different conditions: i. untreated bioplastics (P1 and SB1); ii. AD performed at 37 °C for 30 days (P2 and SB2) in a pilot scale (reactor of 100 L) (Cucina et al., 2021b); iii. P2 and SB2 plus an active composting phase of 15 days (P3 and SB3) (Cucina et al., 2021b); iv. P1 and SB1 after full scale AD performed at 55 °C for 30 days (P4 and SB4) (Cucina et al., 2022a); v. P4 and SB4 plus an AD-maturation stage of the digestate for 40 days at mesophilic conditions (P5 and SB5) (Cucina et al., 2022a); vi. P1 and SB1 after full scale AD performed at 55 °C for 60 days (P6 and SB6) (Cucina et al., 2022b) (Table 1) (see also Supplementary Information).

The tested materials were milled with a blender into pieces of approximately 0.5 cm, which is the size used in standard procedures for aerobic degradability of plastics (EN ISO 17556:2019). Pure microcrystalline cellulose powder (Sigma-Aldrich) was used as the

positive-control reference degradable polymer, while pieces cut from polyethylene (PE) bags were used as a negative reference material.

Table 1. Main operational parameters of anaerobic digestion (AD) biological waste treatment (WT) processes to which the bioplastics PLA and SB have been subjected.

Bioplastic samples	**Sample Name**	**Biological process**		
		Treatment	*SRT* [a]	*Temperature*
PLA	P1	before WT process	/	/
	P2	AD[b]	30	Mesophilic
	P3	AD+Compost[c]	30	
	P4	AD[d]	30	Thermophilic
	P5	AD+Maturation[e]	30	
	P6	AD[f]	60	
SB	SB1	before WT process	/	/
	SB2	AD[b]	30	Mesophilic
	SB3	AD+Compost[c]	30	
	SB4	AD[d]	30	Thermophilic
	SB5	AD+Maturation[e]	30	
	SB6	AD[f]	60	

[a]Solid retention time: the days the solid fraction spent in the AD treatment unit.

[b]After mesophilic anaerobic digestion (Cucina et al., 2021b).

[c]After composting of digestate (Cucina et al., 2021b).

[d]After thermophilic anaerobic digestion (Cucina et al., 2022a).

[e]After maturation phase of digestate (Cucina et al., 2022a).

[f]After thermophilic anaerobic digestion (Cucina et al., 2022b).

2.2 Biodegradation test in soil

Aerobic degradation was performed by soil incubation and was carried out in closed 500 mL glass jars, under aerobic conditions according to standard ISO 17556 (2019). The laboratory scale setup of the experiments, as well as the samples used, are shown in the given figures (see Supplementary Information).

The soil textural composition (dry weight basis) consisted of 700 g kg^{-1} sand, 100 g kg^{-1} clay and 160 g kg^{-1} of natural soil, enriched with compost (40 g kg^{-1}). Soil characteristics (see Supplementary Information) were determined as follows: soil pH in aqueous solution using a 1:2.5 sample/ water ratio, total nitrogen (TKN) by Kjeldahl method, total organic carbon (TOC) by dichromate method (i.e. Walkley-Black method), while the available phosphorus was assessed using the Olsen's method (Olsen S.R and Sommers et al., 1982). Before incubation, the air-dried soil was sieved through < 2 mm particle size mesh and then adjusted with deionized water to bring the moisture to 50% of water holding capacity (100% WHC = 0.305 mL H_2O g^{-1} soil) that was maintained constant through the incubation period (120 d). Mineral salts solution was added to the soil and it consisted of 0.2g KH_2PO_2, 0.1 g $MgSO_4$, 0.4 g $NaNO_3$, 0.2 $CO(NH_2)_2$, and 0.4 NH_4Cl kg^{-1} of soil, accordingly to the standard procedure (ISO 17556:2019).

Two sets of bulk soil samples were made to test the impacts of digestate when applied to the soil incubated with each bioplastic material. Equally sized subsamples of unamended soil (U) and soil amended with digestate (D) were prepared.

The soils (20 g dry weight) with digestate and without digestate were distributed in petri dishes, mixed with the tested bioplastics at 1.25 % w/w solid loading as established by the standard procedure (ISO 17556:2019; Cucina et al., 2021b) and ensuring that the bioplastic

samples added to each glass jar for the incubation were fully in contact with the soil from both sides. The digestate was obtained from the full-scale scale anaerobic digester plant operating a high-solid thermophilic anaerobic digestion (HSAD) and used to produce bioplastic samples P4, SB4, P5 and SB5 (Cucina et al., 2022 a, b). The Plant was located in Lombardy Region (North Italy). The THSAD plant, located in Lombardy Region (northern Italy), transforms different types of wastes, mainly sewage sludge, into a useful soil improver (i.e. digestate) and N-based mineral fertilizer (i.e. ammonium sulphate), i.e. renewable fertilizers, and provides the electrical and thermal energy needs of the plant (Pigoli et al., 2021).

Digestate showed a dry matter (dm) content of 103 ± 3.7 g kg^{-1}, volatile solid of 607 g kg dm^{-1} and a total N concentration of 77 ± 3.7 g kg^{-1} DM ($N\text{-}NH_4^+$/N of 46.6%); more data can be found in Pigoli et al. (2021). The amount of digestate added was chosen to achieve a biomass-bioplastic C/N ratio of 25 corresponding to a rate equivalent to 350 kg N ha^{-1}, considering the soil bulk density of 1 g cm^{-3} and a plough depth of 20 cm, thus analogous to an N field application for typical corn fertilization in the Lombardy Region ~~(North Italy)~~ (Riva et al., 2016). The 24 conditions employed, i.e., 2 bioplastics × 6 bioplastic treatments, each one of them with and without incorporation of digestate were set up in triplicate with controls, i.e., no bioplastic was added to soil, positive (powdered cellulose) and negative (polyethylene) controls, for a total of 64 experimental units.

The soil respiration was monitored by measuring the CO_2 evolution by titration (ISO 16072:2002). In brief, the CO_2 released by the samples was trapped in 0.1M NaOH and titrated with 0.1M HCl, using phenolphthalein as indicator after precipitation of carbonates with 20% $BaCl_2$. The test was conducted in the dark at a controlled temperature of 25 °C and the CO_2 evolved (g kg^{-1}DM) was measured after 2, 9, 15, 28, 35, 55, 70, 82, 90, 100, 120 days from the beginning of the incubation. The results were expressed as % of bioplastic

245 degradation calculated as the cumulative amount of carbon (C) evolved from each sample
246 divided by the amount of C of tested material and then multiplied by 100. Blank
247 measurements using the soil incubated in the absence of bioplastics materials (i.e. control
248 soil) were subtracted from each sample.
249 Furthermore, the degree of biodegradation rates was assessed by the estimations of the kinetic
250 parameters on degradation of these polymers (mg C g C^{-1} d^{-1}), carried out taking into
251 consideration solely the residual C, subtracting from the initial C input, the C that was
252 released and that evolved throughout the course of respiration period, where the initial
253 organic C content in bioplastics was determined according to Springer-Klee method
254 (Springer and Klee, 1954) and the results, i.e. 492±3 mg g dry matter $(dm)^{-1}$ and 533±1 mg g
255 dm^{-1} for PLA and SB bioplastics, respectively, were in accordance with literature
256 (Ebrahimzade et al., 2022; Balaguer et al., 2016; Patnaik et al., 2020; Weng et al., 2013).
257
258 *2.3. Mass balance*
259 Mass balance diagrams for waste treatment during thermophilic and mesophilic AD and
260 composting followed by soil incubation based on 100 g of dry initial bioplastic were
261 constructed. In particular, the bioplastic residual mass after waste treatments was calculated
262 taking into account the degradation (% dry matter) reported previously by Cucina et al.,
263 (2021b) and Cucina et al., (2022). The overall bioplastic degradation was determined from
264 both waste treatments and soil incubation.
265
266 *2.4 Analytical methods*
267 Modification of bioplastics samples after soil incubation were investigated by Fourier
268 transform infrared (FTIR) spectroscopy using a Shimadzu IR Affinity-1S equipped with a

Miracle Pike ATR device (Shimadzu Italia srl, Milano, Italy) with built-in diamond-germanium ATR (attenuated total reflection) single reflection crystal.

The samples were pressed uniformly against the diamond surface and spectra were obtained in triplicate using an average of 32 scans in the NIR range (500–4000 cm^{-1}) with a spectral resolution of 2 cm^{-1}. Air was used as the background. Baseline correction and vector-normalization were conducted using Shimadzu LabSolutions IR software.

The hydrophilic behaviour of PLA and SB bioplastics samples was measured determining the bioplastic wettability by quantifying the water absorption following a standard procedure (ISO 62:2008). Briefly, about 0.1 g of bioplastic samples were placed into a container filled with deionized water at 23 °C. After immersion for 24 h the samples were collected and gently treated with filter paper to remove all surface water. Then the wet samples were reweighed to determine the amount of water absorbed. The wettability (WUC %) of bioplastic samples (i.e. the water uptake capacity) was calculated as follows:

$$\text{WUC (\%)} = \frac{Wf - Wi}{Wi} \times 100$$

where W_f is the bioplastic weight after water immersion while W_i is the initial sample weight.

2.5 Statistical Analysis

Statistical analyses were performed by SPSS software (SPSS Statistics v21.0, IBM, Armonk, NY, USA). Data were analyzed for statistical significance and the difference between mean values was compared using Tukey test. A probability value of $P < 0.05$ (95% confidence level) was considered significant.

3. Results and Discussion

With the goal of assessing biodegradation rates in soil of two bioplastics (i.e., PLA and SB) which had previously been exposed to different pilot and full-scale biological waste treatments as described in Table 1, soil incubation tests were performed, and dynamics of bioplastics degradation were investigated. The impact of digestate when applied to soil on the degradation efficiency of the tested bioplastic materials was also evaluated and the results, assessed from the biodegradation assays, are discussed in the following sections. The first part provides a comparison of biodegradation kinetics of residual bioplastics during soil incubation. The second section presents primary modifications due to bioplastic treatments affecting the overall decomposability along with the mass balance to explain differences in bioplastic degradation performance during waste treatment and soil incubation.

3.1 Soil respiration and kinetic parameters of PLA and SB degradation

The % of biodegradation referred to the initial organic carbon fraction added is shown in Table 2 (see also Supplementary Information). After 120 days of soil incubation 66 ± 2 % w/w and 73±3 % w/w of C evolved from the cellulose powder used as positive reference material in the trials performed without and with the addition of digestate, respectively (Table 2). These results were higher than those reported by Cucina et al. (2021b) i.e. 32.7 % w/w, although those data were obtained in a shorter time, i.e., 90 days of incubation.

The starch-based materials showed rather a low level of degradation in soil and negligible change in biodegradation rates regardless of whether they had undergone AD treatments in mesophilic or thermophilic conditions. Interestingly, the highest degradation rate was found for untreated starch-based polymer (SB1) which degraded after 120 days by nearly 50% w/w (i.e., 49.7±2.5% w/w and 49.1±2.3 % w/w) in both soils tested. These results agreed with values observed previously by Cucina et al., (2021b) who reported for untreated starch-based polymer, comparable mineralization rate after 90 days of soil incubation (i.e. 34 % w/w of C

318 evolved). Moreover, except for SB2 samples, which had undergone the mildest conditions
319 (i.e., mesophilic AD for 30 days), in which degradation reached 21±3 % w/w and 27±0.9 %
320 w/w in soils without and with digestate, respectively, the degradation in all the other treated
321 SB samples was very similar and below 20% w/w (as an average).
322 Conversely, the effect of bioplastic pretreatment was mainly found in soil incubated with
323 PLA samples, that degraded the most where the harshest treatment in terms of temperature-
324 duration during AD had been applied, i.e., P4 < P5< P6 (Table 1). Notably, PLA samples
325 treated under mesophilic conditions (i.e., P2 and P3) behaved similarly to, or even more
326 slowly than the corresponding untreated PLA, in both soils tested (i.e., with and without
327 digestate), indicating the negligible effect that low temperatures during mesophilic AD had in
328 promoting the degradation capacity of this kind of material (Table 2). The biodegradation
329 rates of PLA found here agreed with literature which reported values in the range 10% − 20%
330 w/w (Urayama et al., 2002; Wu, 2012). These results were also in line with previous data that
331 reported, for PLA treated in mesophilic conditions and recovered from compost (i.e., P3),
332 similar degradation rates in comparison with the corresponding untreated samples (Cucina et
333 al., 2021b).
334 Previous reports suggested that the biodegradation of PLA bioplastics blends was linear,
335 indicating a zero kinetic of degradation, i.e. biodegradation did not depend upon bioplastic
336 concentration, and appeared to follow a *take away* mechanism (Cucina et al., 2021b). From
337 calculations, the kinetic constants (k) of biodegradation for PLA treated for 60 days in
338 thermophilic AD conditions (i.e., P6) was of 3.9±0.3 mg C g C^{-1} d^{-1} in soil with digestate and
339 similarly it was of 4.2±0.12 mg C g C^{-1} d^{-1} without digestate addition, which corresponded to
340 256±21 and 239±7 days, respectively, to reach full biodegradation (Table 2).
341

Table 2. Degradation of bioplastics in soil without (SWOD) and with digestate (SWD), and estimation of kinetic parameters of biodegradation.

Bioplastic samples	Sample Name	SWOD			SWD		
		% Biodegradation[a]	**k[b] (mg C g C^{-1} d^{-1})**	**Time for complete degradation [c] (d)**	**% Biodegradation[a]**	**k[b] (mg C g C^{-1} d^{-1})**	**Time for complete degradation[c] (d)**
PLA	*P1*	20±1.4 aA[e]	1.89±0.14aA	530±39cA	20±1.5 aA	1.91±0.15 aA	524±42 cA
	P2	20±0.9 aA	1.87±0.1aA	535±27cB	25±1.7 aB	2.42±0.18 aB	413±32 bA
	P3	20±1.4 aA	1.82±0.13°	549±40cA	23±2.2 aA	2.22±0.24 aA	450±48 bA
	P4	28±1.4 bA	2.87±0.15bA	348±18bA	32±2.8 bA	3.33±0.3bA	301±27 aA
	P5	32±1.4 cA	2.93±0.16bA	341±18bB	36±1.9 bA	3.77±0.19bB	265±13 aA
	P6	39±1.2 dA	4.19±0.12cA	239±7 aA	37±2.8 bA	3.91±0.32bA	256±21 aA
SB	*SB1*	50±2.5dA	5.97±0.4 cA	168±11aA	49±2.3 dA	5.84±0.29 dA	171±9aA
	SB2	21±3.4 cA	2.67±0.21bA	374±29bA	27±0.9 cB	2.69±0.09 cA	372±12bA
	SB3	12±1.8 aA	1.77±0.16aA	565±51cA	20±1.7 abB	1.89±0.17abA	528±47cdA
	SB4	20±1.8 bcA	1.91±0.18aA	524±49cA	18±0.6 abA	1.70±0.05abA	588±19deA
	SB5	15±1.9 abA	1.89±0.20aA	530±56cA	22±2 bB	2.15±0.20bA	466±43cA
	SB6	20±0.9 bcB	1.86±0.09aB	538±26cA	17±0.8 aA	1.62±0.08aA	619±30eB
Control(+)[d]	Cellulose	66±2	8±0.5	123±5	73±3	8±0.5	123±5
Control (-)[d]	PE	1.4±0.2	0.17±0.02	5,990±878	2±0.6	0.29±0.05	3,439±592
Cucina et al. (2021b)[e]	Cellulose	32.7	3.6	138	-	-	-
	PE	0	0	-	-	-	-
	PLA-*P1*	5	0.56	900			
	SB-*SB1*	34.3	3.8	131			

[a]Referred to the initial C content of the tested material dosed in each jar.
[b]Coefficient constants were calculated considering a zero order kinetic for PLA, and both starch and polyester composing SB.
[c]Indirectly estimated assuming a zero order kinetic model see point b.
[d]Cellulose powder and PE plastic were used as positive and negative reference material, respectively.
[e]Data from Cucina et al. (2021b).
[f]Means followed by the same letters are not statistically different according to Tukey test ($P \leq 0.05$): small letters in the same columns are used for differences within bioplastic samples while capital letters are used for differences between soil tested (i.e., with and without digestate) within bioplastic samples.

351 On the other hand, since SB bioplastic samples are composed mainly of both starch (35%)
352 and polyesters (65%), as reported by Cucina et al. (2022a, 2022b), the calculation of kinetic
353 constants of biodegradation of this type of bioplastic needs to take into consideration the
354 contributions of each polymer, thus correcting for the differences in their degradation rates.
355 Since typically a fast degradation occurred for the starch, it was assumed that the C released
356 and evolved throughout the course of respiration from the untreated SB samples was due to
357 the starch decomposition. Confirmation of this came from the untreated SB that, when
358 incubated in soil, showed similar C evolution to that observed from cellulose. Contrarily, it
359 was assumed that after thermophilic AD for 60 days, the C evolved in soil was mostly due the
360 polyester residual fraction that remained after the waste treatment, since the starch had been
361 released earlier during the previous waste processing. This was indeed confirmed from FT-IR
362 results (later discussed in section 3.3) that demonstrated the reduction of starch/polyester
363 ratio, compared with the untreated SB samples (1.28 vs. 0.15).
364 In order to appropriately define experimental kinetic data from soil incubation and to make
365 the comparisons easier, for the SB samples a kinetics was applied by weighting the contribute
366 of starch as well the residue represented mostly by the more recalcitrant polyester portion. To
367 do so, the weighted sum of both kinetics obtained from untreated SB composed of 35% starch
368 and 65% of polyester, and the kinetic obtained from residual SB6, assumed to be composed
369 of nearly 100% of polyester, were considered to estimate the time for complete degradation
370 in soil of SB residual bioplastic samples. From the results, untreated SB samples were
371 expected to complete their degradation after 330 ±23 days in soil without digestate and
372 similarly after 310±16 days in soil with digestate (Table 2) (Figure 1). On the other hand,
373 pretreated SB degraded similarly independently of AD temperature and pretreatment time,
374 i.e., in 174-183 days (Table 2) (Figure1).
375

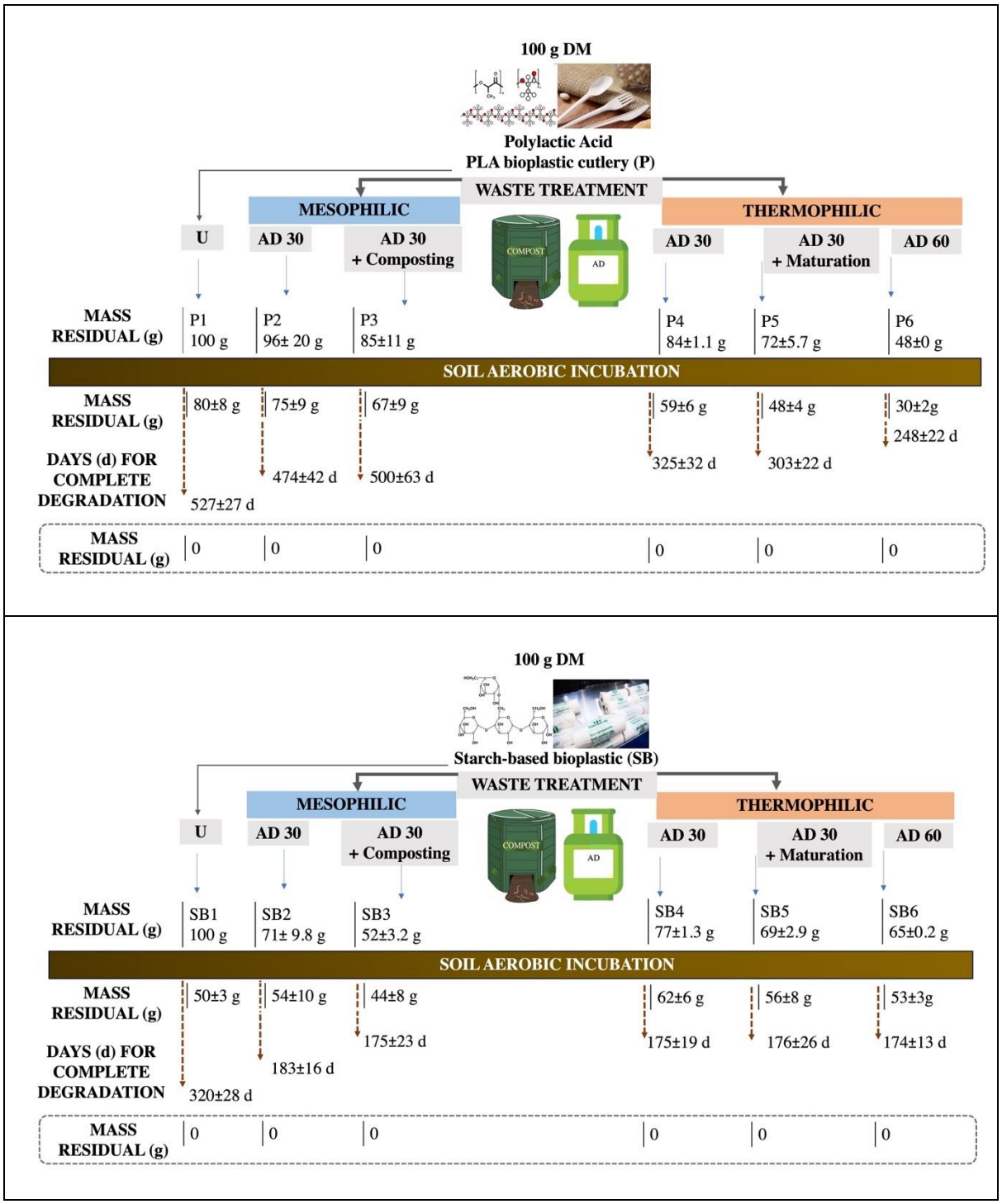

Figure 1 Mass balance for degradation of bioplastic untreated (U) PLA (top) and SB (bottom) and after the waste treatment processes under mesophilic and thermophilic conditions, followed by incubation in soils with and without digestate (averaged).

3.2 Soil respiration: effect of digestate addition on biodegradation of bioplastics in soil

382 The organic carbon from the digestate is reported to be available when added to soil leading
383 to maintaining soil biological activity (Verdi et al., 2019), bringing possible advantages for
384 bioplastic degradation. Results (Table 2) (Supplementary Information) showed that the effect
385 of digestate application on rates of bioplastic degradation was minimal, with soils having
386 very similar respiration and only a few differences were found, in the soils incubated with P2
387 and P5, where the bioplastic degradation was slightly greater in soil with the digestate
388 addition than for the soil where it was not added. However, the differences may have
389 occurred randomly rather than being attributable to the digestate addition. This was also
390 observed for soils incubated with SB samples, where only samples SB2, SB3, SB5 showed
391 slightly more C evolved from soil with digestate. Based on the results obtained, the use of
392 digestate was not associated with any major improvements in terms of the degree of
393 bioplastic degradation, since no effect on the C evolution during the experimentation was
394 observed.
395
396 *3.3 Main substrate features of bioplastics inducing overall degradation*
397 In this study, SB and PLA samples behaved significantly differently during their incubation
398 in soil where a slower degradation characterized the untreated PLA samples, compared to the
399 treated PLA; the opposite was found for the SB samples, which, if untreated, degraded at a
400 faster rate than the treated ones (Table 2). It may seems counterintuitive that SB samples after
401 biological treatment decomposed more slowly than the untreated SB samples. The
402 explanation of this behavior is that treated SB samples has been subjected during the AD
403 biological process to the partial removal of the most amenable fraction (i.e. starch), thus the
404 residue was the most recalcitrant part (polyester) with higher resistance to degradation when
405 incubated in the soil.

406 This was not surprising because of the inherent biodegradability of the starch which ~~was~~
407 preferentially consumed in the untreated SB samples compared to those which had undergone
408 AD and composting treatments, in which their partial degradation had already taken place,
409 with a consequent concentration of the more recalcitrant and slower component to degrade
410 (polyester), as previously suggested (Cucina et al., 2021b).
411 This was confirmed by FT-IR analysis, which was used to evaluate changes in bioplastics'
412 composition during the different treatments as well after the soil incubation (Table 3).
413 With regard to SB materials, the chemical changes were observed specifically by observing
414 FT-IR starch and polyester bands at 1050 and 1720 cm^{-1} respectively (Cucina et al., 2021b).
415 The modifications occurring during waste treatments of SB samples confirmed previous
416 results (Cucina et al., 2021b). The untreated SB samples (SB1) showed levels of starch and
417 polyester resulting in a ratio of 1.28 (Table 3). When compared to the untreated samples, a
418 significant increase of band intensities of polyester (1720 cm^{-1}) were observed in all
419 bioplastic samples which had undergone biological treatments, resulting in a decreased ratio
420 (i.e. starch/polyester) of peaks areas of 4 to 8 times compared to that observed for the
421 untreated material, due to the consumption of starch (Table 3).
422 Interestingly the starch/polyester ratio decreased with the severity of the biological treatments
423 in term of temperatures and time, thus revealing that thermophilic conditions during AD and
424 longer time led to greatly decreased starch presence in SB samples compared to those
425 exposed to AD under mesophilic conditions and shorter time. The strong negative correlation
426 found for starch/polyester ratio vs. degradation ($r= -0.81$, $p<0.05$, $n=6$) confirmed that
427 degradation of SB materials started preferentially from the starch, corroborating the
428 concentration effect of the elimination of starch molecules, as previously shown (Cucina et
429 al., 2021b). When incubated in soil, the behavior of such residual SB samples indicated an
430 evolution of spectra only for the untreated sample (SB1), which showed a decrease of the

diagnostic peak of starch and consequently starch/polyesters ratio below 0.5 in both soils tested (Table 5). These results agreed with the observed degradation values which were in fact higher in the soil incubated with the untreated sample (SB1), than the degradation observed in the soils with all the other tested residues. These findings confirmed how easy it is for starch present in such types of bioplastic samples to degrade, and also its preferential consumption by the microorganisms present in the soil. Few changes in the starch/polyester ratio were observed after soil degradation of the treated samples, hence the absence of correlation occurring in soil between degradation and starch/polyester ratio. Also, the results calculated on the mass basis indicated the absence of significant modifications in the soil, with the starch/polyester ratios remaining almost unchanged for treated SB residues, which evidently had previously (i.e., during waste treatments) lost most of their starch content, as indicated earlier.

Table 3. Chemical modifications of the PLA (P) and starch based (SB) samples after waste treatments (WT) and successive incubation in soil without (SWOD) and with digestate (SWD). Chemical changes observed by measurement of water uptake capacity (WUC%) and by diagnostic FT-IR peaks of crystallinity (CrI) and starch polyester samples for PLA and SB samples respectively.

Parameter	Treatment Assessment	P1	P2	P3	P4	P5	P6
WUC (%)[a]	WT	2.8±0.6	4.8±1.3	5.3±0.9	16.5±2	51.9±5	50.1±10
CrI[b]	WT	0.67	0.64	0.59	0.51	0.52	0.40
	SWOD	0.71	0.65	0.67	0.67	0.50	0.53
	SWD	0.74	0.58	0.68	0.67	0.59	0.49
		SB1	**SB2**	**SB3**	**SB4**	**SB5**	**SB6**
Starch/polyester[c]	WT	1.28	0.34	0.36	0.47	0.22	0.15
	SWOD	0.19	0.67	0.65	0.36	0.13	0.24
	SWD	0.39	0.47	0.62	0.22	0.16	0.20

[a] Determined according to standard procedure ISO 62:2008.

[b]Ratio between diagnostic peaks area at 755 cm^{1} and 870 cm^{1} crystalline and amorphous regions respectively (Stoleru et al., 2017).

[c]Ratio between diagnostic peaks area at 1050 cm^{1} and 1720 cm^{1} starch and polyester regions respectively (Stoleru et al., 2017).

With regard to PLA materials, the chemical changes were measured in terms of crystallinity (CrI) and amorphous portions, which have been reported to affect degradation efficiency (Bandini et al., 2022; Pathak et al., 2014). A comparison of CrI values obtained by observing FT-IR crystalline and amorphous bands at 755 and 870 cm^{-1} respectively (Stoleru et al., 2017) is reported in Table 3. The untreated PLA samples (P1) showed the highest levels of crystalline portion, resulting in CrI ratio of 0.67. Compared to the untreated sample, a significant decrease in the intensity of the crystalline band (755 cm^{-1}) was observed in all the treated samples, which, with the severity of treatments in term of temperatures and time, reduced this portion (Table 3). The results revealed that thermophilic conditions during AD (P4 and P5) and a longer retention time at high temperature (P6), led to an increase of the amorphous portion in PLA samples compared to those exposed to AD under mesophilic conditions and shorter time. The strong negative correlation found between CrI vs. degradation ($r=0.95$, $P<0.05$, $n=6$) confirmed the key role of this factor in the degradation of

semi-crystalline materials such as PLA bioplastics. Therefore, when the treatment of PLA exceeded its glass transition temperature (i.e., 55-60 °C), this evidently increased the amorphous portion and thus changed the physico-chemical properties, increasing the subsequent degradation.

Bioplastic characteristics that affect the rate of biodegradation also include chemical and physical properties of the surface. Therefore, characteristics such as hydrophilic and hydrophobic character were estimated for the tested samples to gain information about the effect of such properties on decomposition in soils and determine the mechanism underlying biodegradation of such residual bioplastics.

The hydrophobicity was determined by detecting the bioplastic wettability (WCU), i.e., the ability of solid surface to be wetted when in contact with water. Results indicated the following rank in terms of WUC (%): P6=P5>>P4 >P3=P2> P1; thus, the untreated PLA was characterized by the lowest WUC % (Table 3). Different WUC % values reflected the hydrophobic character of these polymers, with the treated PLA being more capable of binding water than both untreated PLA and those samples subjected to AD under mild mesophilic conditions. In particular, the differences in hydrophobicity that characterized the samples may have influenced the behavior in soil, as confirmed by the good correlation between WUC (%) and degradability rates tested in soils without digestates ($r=0.86$; $P < 0.01$; $n=6$) and with digestate ($r = 0.92$; $P < 0.01$; $n=6$). It was reported that hydrophilicity of bioplastic surfaces favors interaction with moisture and microorganisms' activity (Vasile, 2018).

The higher biodegradation rates found in this work could be explained by the fact that the AD process treatment allowed the molecules composing PLA to have higher affinity with water and thus to become more amenable to microbial enzymatic attacks. Therefore, it can be understood that the increase in polymer hydrophilicity arising from the treatment to which the

494 PLAs had been subjected, played a key role in determining high susceptibility to
495 biodegradation in soil. These results agreed with crystallinity values obtained from FT-IR. As
496 earlier mentioned, the untreated PLA showed the highest crystalline value indicating its
497 densely organized and bonded macromolecule chains, that likely prevented water from
498 accessing the polymer network, thus in turn, delaying and slowing the biodegradation in soil
499 (Xue et al., 2019).
500 After anaerobic incubation, the crystallinity values decreased compared to the initial polymer
501 from 0.67 to 0.40, with the PLA after the harshest treatment (i.e., P6) being much lower than
502 that recorded in samples treated under mesophilic conditions. These results seem to confirm
503 the contribution of crystallinity to degradation, in agreement with literature that reported that
504 the lower percentage of crystalline structure in AD-treated polymers was associated with
505 higher water solubility which increased and greatly favored the possibility of biopolymer
506 degradation (Peng et al., 2022; Antunes et al., 2021), as shown by the strong negative
507 correlation observed between WUC (%) and CrI ($r=-0.8$; $P< 0.05$; $n=6$).
508
509 *3.4 Material balance of the entire conversion process: degradation of PLA and SB from*
510 *waste treatment to soil*
511 As previously reported, during the waste management treatments, bioplastic samples were
512 degraded to different degrees (Cucina et al., 2022; Cucina et al., 2021b). Data from the
513 overall process were collected and analyzed and a complete mass balance, referred to 100 g
514 of bioplastic, including biological treatments (AD and composting) followed by soil
515 incubation, was schematized in Figure 1, and reported in Supplementary Information, where
516 bioplastic residual contents were normalized to initial bioplastics.
517 A strong effect of severity of treatment in terms of both temperature and its duration on the
518 bioplastic degradation was observed in PLA materials. In particular, at mesophilic conditions

519 of AD, the degradation was only of ~3.3% and below 15% for P2 and P3, while after
520 thermophilic settings the degradation reached 52% (P6). The same trend of PLA degradation
521 was reflected in soil albeit to a lesser extent compared to the behavior in the digesters but was
522 still significant. The differences were however much more marked when the degradation of
523 PLA residues from the overall process was considered, reaching a degradation of the whole
524 process (i.e., considering both waste treatment and soil) in the order of 70% (Figure 1)
525 (Supplementary Information), indicating that thermophilic digestion can efficiently promote
526 modifications and thus physicochemical properties that render this biopolymer more
527 amenable for biodegradation in soil. However, when comparing the extent of the degradation
528 rates on the same samples subjected first to digesters and then to incubation in soil, a lower
529 rate of increase and lower variation in degradation in those samples treated at more severe
530 conditions was observed. This result indicated that probably the soil, even if PLA had not
531 been treated under severe conditions, may have promoted a certain level of their degradation
532 that did not occur in the samples already treated and previously degraded in digesters at
533 moderate thermophilic temperatures.
534 The rankings for biodegradation performance of PLA samples, almost identical in both soils
535 tested, and the findings observed in terms of mass balance, confirmed that thermophilic
536 temperatures applied to PLA during AD led to multiple benefits.
537 In particular, the thermophilic approach tested (i.e., AD at 55 °C for 60 days) enhanced
538 renewable biogas energy production yields, while obtaining a high rate of PLA degradation
539 that benefits soil, providing a good quality digestate and compost with reduced leakage of
540 PLA mass, that eventually could reach the full degradation in less than a year (i.e., 248 ±22
541 days on average) when incorporated into the soil. Furthermore, even if only small differences
542 in degradation rates in soil of thermophilic treated residual PLA (P4 and P5) were found, it is
543 important to note that these samples showed, compared to P6, much lower biogas yields and

degradation during the AD conversion processes, therefore such routes, in addition to not being energetically desirable, were also unable to effectively reduce bioplastics' potential leakage into compost and digestate from waste management.

The mass balances considering the entire process to which the SB bioplastics have been subjected, showed that degradation of nearly 50% on the starting material can be achieved, regardless of the waste treatment (Figure 1) (Supplementary Information).

Different conclusions can be drawn from examining the mass balance and results obtained from SB samples for which the temperature of prior processing had minimal effects. In particular, the application of mesophilic or thermophilic approaches allowed similar degradation yields during AD processes, thus achieving comparable, unfortunately not very high biogas yields, while sending off a mass residual processed SB that in the subsequent incubation in soil completed degradation similarly in less than 200 days. A higher degradation was observed when composting followed AD (SB3), however the approaches that allowed the better energy recovery could be considered more advantageous from the circular perspective. In summary, and as discussed above, the low degradability both in AD and in the soil found for the SB materials, could be ascribed to the different polymers that form this type of bioplastic which, in addition to starch, is composed of polyesters that are relatively resistant to degradation. Conversely for PLA, as described, the severity during the waste management treatments, which modified its structure, influenced its amenability which resulted in superior biodegradation.

Conclusion

This work reported the results of the first attempt to evaluate the degradation of different bioplastics items in soil after they had been subjected to mesophilic or thermophilic AD and

569 composting treatments. The results obtained were well replicated in both soils tested with and
570 without the addition of digestate. Considering the whole process (i.e., both waste treatment
571 and subsequent soil incubation) the best performance approach, combining energy production
572 (biomethane) and bioplastic degradation resulting in highest degradation rates of bioplastics,
573 were that SB bioplastics degraded by 50% at the end of the experiments, while PLA achieved
574 overall degradation of 70% when thermophilic temperatures had been applied for 60 days.
575 Kinetics calculated from experimental data indicated that residual bioplastic after waste
576 treatment potentially degraded completely after 248-500 days and 174-183 days, respectively
577 for PLA and starch-based bioplastics.
578 The study provides evidence of the potential of such AD and composting integrated schemes
579 for the conversion of bioplastics within the OFMSW for the realization of efficient
580 bioconversion systems into the logic of the circular economy model, where the bioplastic
581 recycling appropriate end-of-life pathways and waste management routes prevent bioplastic
582 accumulation, while recovering valuable composted outputs beside energy (biomethane). The
583 use of bioplastic in AD has, also, a great effect on life cycle GHG emissions, i.e. bioplastic C
584 transformed into biomethane allows replacing fossil C, reducing the bioplastic C footprint.
585 This fact depends significantly upon the degradation rate of bioplastic during AD, i.e. high
586 degradation produces more biomethane reducing the CO_2 produced in soil because of residual
587 bioplastic degradation. Therefore producing biomethane reduced the C footprint, since in situ
588 CO_2 recovery, i.e. the capture of CO_2 coming from bioplastic degradation in soil, is very
589 difficult to perform. [Or, frankly, impossible!]
590 The insights gained will contribute to understanding the biodegradation processes in both
591 engineered and natural environments and contribute towards the implementation of optimized
592 measures and waste-management policies.
593

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