Numerical analysis to predict bioplastic biodegradation with FORSU in an integrated anaerobic and composting process

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Keywords: bioplastics, anaerobic digestion, composting, modeling.
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Due to the sharp increase in the production and diffusion of plastics around the world, a shift in the world of plastics production bioplastics is underway. The speed of the shift is rather slow, but it is estimated that by 2030, 2.3 to 7.6 million tons of bioplastics will be produced (European Bioplastics, 2021). In this regard, the European Parliament passed a law in 2019 banning the use of various single-use items by 2021, which will be gradually replaced with similar versions made of biodegradable material (European Parliament, 2019). It is crucial to distinguish the different types of bioplastics: bio-based biodegradable, non-bio-based biodegradable, and bio-based non-biodegradable (European Bioplastics, 2018).

Regarding the degradation of bioplastics, three aspects are identified in standards and scientific studies (F.Ruggero et al., 2021): biodegradability, disintegration and compost quality. Disintegration is the physical decomposition of a material into small fragments (M.P.Balaguer et al., 2016) and is usually investigated using the standardized methods EN 14806, ISO 20200 (F.Ruggero et al., 2021) whereas biodegradability is defined by the technical standards UNI EN 13432:2002 for packaging items and UNI EN 14995:2007 for other materials.

UNI EN 13432 certified biodegradable bioplastics today are collected with the organic fraction of municipal solid waste (European Parliament, 2018). They are then subjected to biodegradation processes such as composting and anaerobic digestion, producing compost, biogas, and digestate, respectively. To ensure degradation within legal limits, it must be ensured that certain conditions are met, and that everything that goes in is biodegradable under those conditions. In order to reduce the possibility of finding at the end of composting or anaerobic digestion, contaminants in the final products (compost or digestate), several rules have been introduced (F.Ruggero et al., 2019). It was necessary to introduce regulations in the field of degradation of bioplastics to assess their degradation kinetics as a function of operational parameters to be able to determine whether they are suitable for undergoing such processes (UNI EN 13432; UNI EN 14995). Tests performed to assess degradability are on a laboratory scale, where all parameters can be well controlled. But in real plants, fluctuations in parameters such as temperature can vary greatly point by point, leading even to possible inhibition of reactions.

So, it is crucial to know the feedstock input, from volatile content to crystal structure, to definitively indicate whether a certain artifact is suitable to be included along with the organic fraction. Conflicting opinions related to the effective biodegradation of certain materials, such as starch-based bioplastics like PLA, can be found in the literature. Considerably longer retention times are needed for PLA to biodegrade under anaerobic digester system conditions, making it unsuitable for anaerobic digestion (S.Vardar et al., 2022). Even if PLA is often indicated as a material having a biocompatible nature among the bioplastics, the methane production was characterized by a lag phase of about 10 days, not comparable with the lag phase of the digesters treating of OFSMW, whose degradation starts in few hours (F.Battista et al., 2021). Large scale anaerobic digestion shows that PLA bottles didn't biodegrade under anaerobic conditions and the pieces appeared wrap up after 23 days (F.Bandini et al., 2020).

In addition to the chemical composition of a material, so many aspects count, such as surface area-to-volume ratio, crystal structure, and others. So, it is difficult to assess a material solely based on its elemental composition. In this work, the biodegradation of materials such as PLA with a specific degree of crystallinity and specific surface area was evaluated.

The evaluation is done by numerical simulations using Aspen Plus software, a simulation environment that allows for rapid assessment, the fate of bioplastics as a function of key operational parameters such as temperature, residence time, and reaction kinetics. Biodegradation was studied in terms of integrated aerobic and anaerobic treatment. The developed model uses Polyntrl as the working method and takes as input the chemical compounds present within the organic fraction of municipal solid waste, along with the bioplastics. The latter, analyzed individually together with the FORSU, are defined by means of the CHNS analysis carried out in the laboratory, thanks to which it was possible to go to define the chemical formula and therefore the molecular weight. Regarding FORSU (excluding bioplastics), in the anaerobic digestion stage, the input substrate was considered to consist of: carbohydrates, fats and proteins. The model includes mass transfer reactions involving transfer between gas and liquid phases (W.A.Menacho et al., 2022). This process is simulated using a CSTR reactor. Carbohydrates were incorporated as cellulose, starch, and hemicellulose. Proteins were added according to their solubility as soluble and insoluble proteins. Fats consisted of tripalmate, triolein, palmito-olein, and palmito-linolein. The first hydrolysis step takes place in a first reactor, as it is the slowest step; in addition, this separation serves to show the effect of any pretreatment on the speed of the hydrolysis step. The reactions are defined by the degree of reaction and thus a stoichiometric reactor was used, while the other three phases, namely acidogenesis, acetogenesis and methanogenesis are defined by the reaction kinetic constant and thus by CSTR.

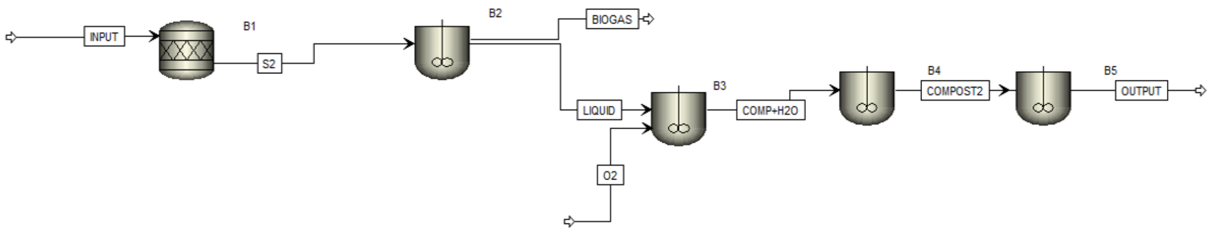

Figura 1. Integrated process layout

Regarding the degradation of bioplastics during anaerobic digestion, it occurs only in CSTR (B2). The overall reaction involving PLA is as follows:

$$PLA + 3H_2O \rightarrow 2CO_2 + 3CH_4 \qquad (1)$$

Since several tests show a linear trend in the anaerobic degradation of PLA, the reaction kinetics are of pseudo-zero order, thus eliminating the dependence on the amount of bioplastic. To calculate the reaction kinetics, the average value of the kinetic constants of degradation under thermophilic and then mesophilic conditions was taken, calculated as the slope of the trend of CO_2 and CH_4 production over time (k_{ad}=0.015 day^{-1}).

Everything that comes out of reactor B2, is divided into two parts: biogas (CH_4 and CO_2) and digestate along with the residue, destined for composting. The latter phase was divided into three sections, corresponding to thermophilic (7 days) and mesophilic conditions (21 days) plus the last maturation phase at room temperature (60 days). Again, kinetic constants were calculated as the slope of the curve of g CO_2 /g CO_{2th} produced versus time (M.Avaara et al., 2001), as it corresponds to the amount of fully degraded carbon in the residual PLA.

The results in the table show the percentage of PLA degradation, and for the same residence time of the anaerobic phase (the aerobic phase has fixed times), increasing the temperature leads to more degradation, up to 60 percent.

Tabella 1. PLA degradation results of integrated process

Temperature (°C)	**Residence time (day)**	**Total degradation (%)**
37	15	24
37	30	26
37	60	28
55	15	37
55	30	53
55	60	60

The work presented showcases what the potential of integrated aerobic/anaerobic treatment is and illustrates how degradation levels are not very high, despite the rather stringent conditions in the case of 55°C digestion and 60 days residence time. Moreover, these conditions are difficult to ensure within large-scale plants, and this can result in reduced temperatures to the point of process inhibition.

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