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To the best of the authors knowledge, there has not been any study done which compares biodegradability in real and simulated conditions. This paper investigates and compares the biodegradability of polylactide (PLA) bottles under different testing methods of existing standards, standards under development, and a novel method of evaluating biodegradability of biodegradable materials under real composting conditions.

1. Métodos

usan botellas PLA comerciales y lo analizaron/biodegradaron con 3 métodos: compost común, CMR y GMR

Compost real: The biodegradation study was carried out for 30 days. The dimension of the pile was 6 m in width, 24 m long, and 3 m in height, and it was built on an asphalt pad. The initial temperature, relative humidity, and pH of pile were 65+-5°C, 63+-5 %, and 8.5+-0.5. A wooden box of dimensions 0.6 m 0.3 m 0.1 m was built with a mesh bottom to retain and easily identify the samples and the surrounding compost for further analysis. Initially, compost was added on the bottom mesh, and later the PLA bottle was placed on it and completely covered with compost. The box was placed approximately 1.2 m above the ground and 1 m inside the compost pile where a uniform composting temperature of 65°C was obtained periodicamente hicieron analisis sobre el peso y fotografiaron

Cumulative measurement respirometric (CMR) system This system was designed to yield the percentage of carbon dioxide from the organic carbon content of the sample. The compost was sieved through a 5 mm sieve and inert materials such as glass, stones, and metal were removed. PLA bottles were cut into 0.01 m x 0.01 m pieces (excluding part of the neck and cap threads) to be used as samples for biodegradability evaluation. Cellulose powder obtained from Sigma-Aldrich (Milwaukee, WI) was used as the known reference material (i.e., positive control) The current system is comprised of nine bioreactors; three blanks, three positive controls (cellulose), and three samples (PLA bottles) placed in a temperature controlled system—an environmentally controlled room manufactured by Lab-Line Instruments Inc.

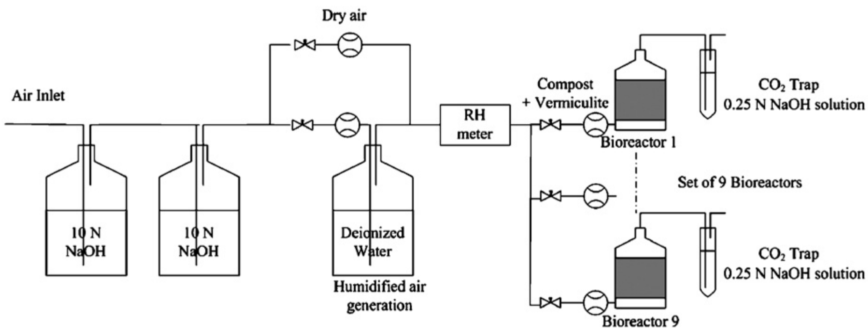


Figura 1: Esquema del CMR.

Initially, pressurized air of 2 psi was passed through 10N sodium hydroxide (NaOH) solution to remove the CO 2 present in the air. Later, the air was passed through deionized water to humidify and maintain uniform moisture level during the experiment of between 50 % and 60 %. The air was divided and passed through flowmeters for each bioreactor at a flow rate of 60 mL/min. A solution with 200 mL 0.25N NaOH was used for trapping the CO 2 from the bioreactors, and the amount of CO 2 content in solution was calculated through acid–base titration. NaOH solution was changed every time that CO 2 was calculated. Ten milliliter aliquots were removed from the 200 mL trapping NaOH solution and titrated with 0.186N hydrochloric acid (HCl) solution to obtain the value of CO 2 in solution. The

CO_2 content in the 10 mL solution was correlated to the 200 mL solution and actual CO_2 amount was determined. The CO_2 trapping reaction was done in a two step reaction as described in ASTM D5338 and mentioned below:

$$NaOH + CO_2 \rightarrow NaHCO_3 \quad \text{then} \quad NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$$

Similarly, during titration CO_2 is removed through the following reactions:

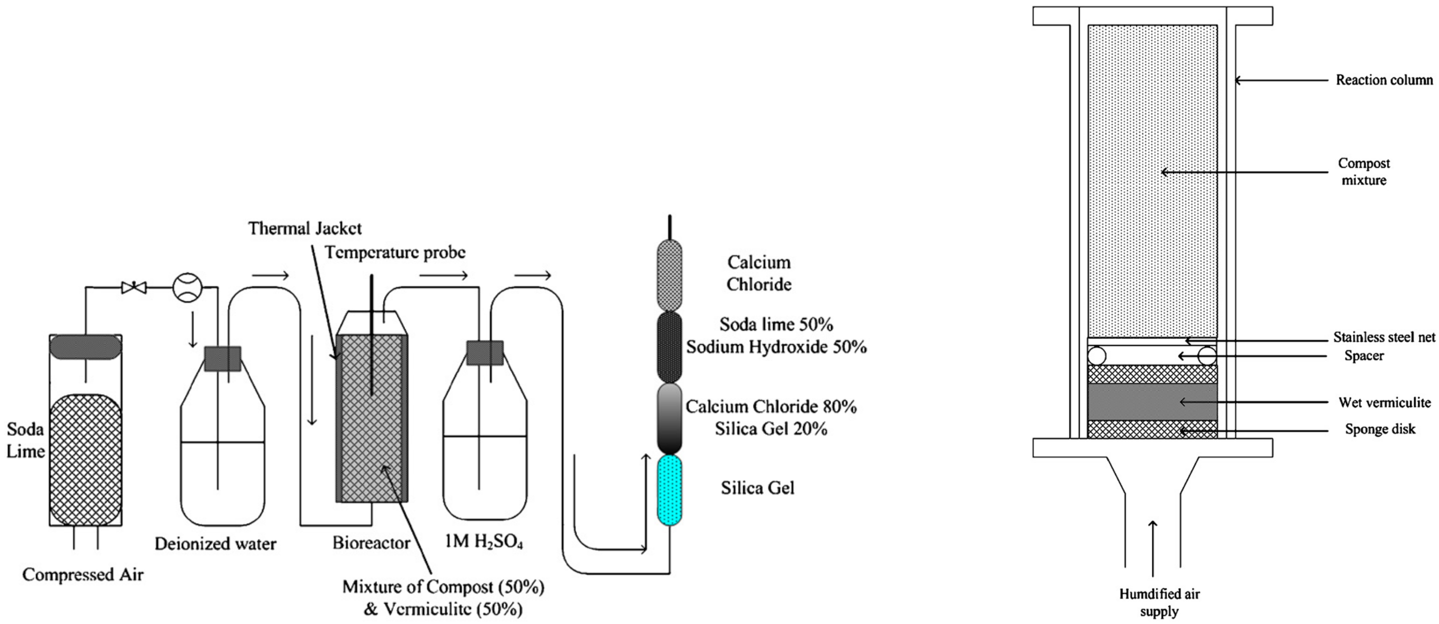
$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl \quad \text{then} \quad NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

Luego hallaron la evolución del CO_2 y mineralizaciones con indicadores de pH y unas ecuaciones

Gravimetric measurement respirometric (GMR) system:

The GMR system construction is based on draft ISO 14855-2 (recommends using two blanks, two positive reference materials, and two samples to be analyzed for the biodegradation measurement) a 1:10 ratio of compost/sample is used A GMR system according to some of these specifications has been built by Hissan Trading Co. Ltd. (Tokyo, Japan), and is commercialized under the name of microbial oxidative degradation analyzer (MODA) which consists of four bioreactors, one for blank, one for positive control (cellulose), and two for samples.

Similar to the CMR, in the MODA system pressurized air is passed through a column containing soda lime with CO_2 absorption indicator from Sigma-Aldrich to make it CO_2 free. Later, the air is bubbled through a flask containing deionized water to maintain the humidity in the compost mixture and in the reaction column constant. The reaction column consists of a column covered with a heating jacket and a thermosensor to maintain the temperature at 58°C. Air is passed through each bioreactor and later through an ammonia eliminator, moisture remover, and finally to a CO_2 trap column. The standard test soil for the MODA system was a mixture of mature compost as previously described for the CMR system (60 g dry weight) and vermiculite (60 g dry weight). Initially the moisture was adjusted up to 90 % of its water holding capacity. Vermiculite (18 g dry weight) was also added at the bottom of the reaction column to absorb the water drips from the compost and also provide equal aeration to the compost mixture. The vermiculite and compost mixture were separated by sponge disks and stainless disk net as shown in Fig. 5. The reaction column was closed with a lid having an attached thermosensor which stayed in contact with the compost mixture. The reaction column was covered with a thermal jacket at a temperature of 58°C, which was continuously controlling the compost mixture. In addition to the carbon dioxide, ammonia and water were also generated from the reaction column which was eliminated by passing the output of the reactors through 2N sulfuric acid (H_2SO_4) in the ammonia absorption flask, and the neutralization of ammonia by H_2SO_4 was monitored by methyl red. Later, the air was passed through moisture removal columns 1 and 2 as shown in Fig. 4. Silica gel (type 3) was used for moisture removal (column 1); when the silica gel was saturated due to moisture it changed color from dark blue to colorless. Moisture removal column 2 consisted of 20 % silica gel and 80 % of calcium chloride (93 % granular, anhydrous) which completely removes moisture from the air. Column 3 was a carbon dioxide absorption column and contains a mixture of soda lime (cica reagent) and sodium hydroxide (1.6–3 mm pellets) at 1:1 ratio. This chemical reaction generated water; hence, column 4 containing calcium chloride collected the remaining water from the reaction. The CO_2 generated by biodegradation in the reaction column was measured by the weight gain seen in columns 3 and 4. The MODA system is a closed system; however, the compost mixture was taken out twice a week for manual turning to ensure proper mixing of compost and sample, and also to improve aeration and maintain accurate moisture in the mixture.



(a) aaa

(b)

Figura 2: esquema del GMR, a la izq la explicación detallada del bioreactor

2. Resultados

REAL COMPOSTING CONDITIONS: On the 15th day, the bottle was already in pieces and mostly consisted of parts from cap threads, neck, and bottle (bottle parts having higher thickness). On the 13th day(creo que quiso decir 30), only a few pieces of bottle were bserved and the majority were from cap threads. After that, no bottle residuals could be located through visual inspection. PLA degradation starts by a hydrolysis reaction, que sigue un decaimiento exponencial el peso moelcular

CMR: la biodegradación del cellulose powder and PLA bottles mostró una mineralización del 60 % en el día 30 y 39 respectivamente. En el día 58 alcanzaron 86 % y 84 % respectivamente. Ambos siguen funciones kinda logaritmicas, coincidiendo al final en el dia 58. Initial slower mineralization action in PLA is due to the fact that it first undergoes hydrolysis, which is a non-enzymatic reaction decreasing the molecular weight and later low molecular weight oligomers are consumed by microorganisms to evolve carbon dioxide.

GMR: cellulose reached 70 % biodegradation value on the 55th day. One of the PLA bottles showed negative biodegradation in the beginning which could be due to few reasons: (a) PLA bottles first undergo hydrolysis which is non-enzymatic reaction; (b) PLA bottles consisted of a bluetone additive and also a label adhesive which may have affected the microbial activity; and (c) the homogeneity of the compost, which makes the compost generate different background of CO2 . Sin embargo, las botellas PLA alcanzaron más del 70 % mineralización al día 52 so we can conclude that PLA bottles are biodegradable according to the ISO 14855-2, but only if all the ISO 14855-2 conditions of number of samples and validity criteria are met (which is not true in this case with the MODA system). On the 25th day, 15 g (dry weight) fresh compost was added to all reaction columns to improve the microbial activity, and an increase in mineralization value can be observed in the graph.

Comparaciones in real composting conditions, the entire bottle was tested, whereas in the CMR system the whole bottle (25 g) was tested but cut into 0.01 m x 0.01 m pieces. Therefore, the higher surface area of the samples introduced in the CMR system should reduce the overall degradation period; however, since the ratio compost/sample was larger in the real composting conditions, a faster degradation process of the bottles was observed. In the case of the MODA system where these two factors (i.e., sample size and compost/sample ratio) were lower than the real composting conditions, an even slower degradation process was observed

Algunas cosas que influeyn en la velocidad de biodegradación también es la cantidad de compost (porque habrían más microorganismos), la cantidad de oxígeno (que sacudieron algunos frascos), la composición del compost tipo de dónde proviene, el tamaño de las muestras de plástico (*)

Standards such as ASTM D5338 and ISO 14855- 1 & 2 provide a traditional way of testing plastics in respirometric systems such as DMR, CMR, and GMR, but they are limited to the plastic material and not to the whole package. However, they do recommend considering the part of higher thickness from the package and evaluate its biodegradability, which can then be used to conclude if a package is biodegradable or not.

3. conclusiones

Real conditions showed degradation of the PLA bottles and variation in their molecular weight as a result of hydrolysis plus biodegradation.

When shredded packages are used in real composting conditions, as used in the CMR or the GMR systems, a faster degradation time could be expected. However, an overall conclusion cannot be exclusively derived based on the sample size, and all the variables in real composting, such as compost raw materials, enzymes, ambient atmosphere, etc. and their interaction with the biodegradable packages, should be explored for better understanding and insight of the biodegradation process (supongo que esto es por *, de ser así nada, chotísimo porque me la re baja jajaja siento que es tirar el paper a la basura).

Current standard methodologies ASTM D5338 and ISO 14855-1 provide a traditional way of testing plastics in respirometric systems, but they are limited to the plastic material and not to the whole package. (al leer esto entendí por qué hacen esto lol)

The new GMR system similarly has limitations of using a small quantity of compost which might extend the period of biodegradation.

In short, current standards mainly answer the question: is a plastic or package biodegradable? But they do not address the final question: will the package successfully biodegrade in a commercial compost facility? Therefore, it is important to test the biodegradation of the complete package under real composting conditions for its efficient deployment in the existing composting processes as demonstrated in this work. (me encantó esto último)