Chemosphere 175 (2017) 452–458

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Assessing the biodegradability of microparticles disposed down the drain

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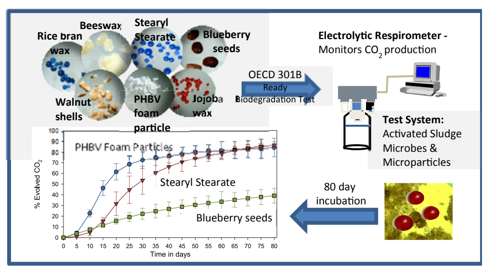
HIGHLIGHTS

- OECD 301B Ready Biodegradation method adapted for non-soluble microparticles.
- Significant mineralization observed for PHBV foam microparticles.
- Significant mineralization jojoba wax, beeswax, rice bran wax, stearyl stearate.
- Blueberry seeds and walnut shells limited mineralization at study completion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 December 2016
Received in revised form
7 February 2017
Accepted 16 February 2017
Available online 20 February 2017

Handling Editor: Tamara S. Galloway

Keywords:
Biodegradation
Microparticles
Down the drain
PHBV foam
Natural materials

ABSTRACT

Microparticles made from naturally occurring materials or biodegradable plastics such as poly(3-hydroxy butyrate)-co-(3-hydroxy valerate), PHBV, are being evaluated as alternatives to microplastics in personal care product applications but limited data is available on their ultimate biodegradability (mineralization) in down the drain environmental compartments. An OECD 301B Ready Biodegradation Test was used to quantify ultimate biodegradability of microparticles made of PHBV foam, jojoba wax, beeswax, rice bran wax, stearyl stearate, blueberry seeds and walnut shells. PHBV polymer was ready biodegradable reaching 65.4 ± 4.1% evolved CO_2 in 5 d and 90.5 ± 3.1% evolved CO_2 in 80 d. PHBV foam microparticles (125–500 μm) were mineralized extensively with >66% CO_2 evolution in 28 d and >82% CO_2 evolution in 80 d. PHBV foam microparticles were mineralized at a similar rate and extent as microparticles made of jojoba wax, beeswax, rice bran wax, and stearyl stearate which reached 84.8 ± 4.8, 84.9 ± 2.2, 82.7 ± 4.7, and 86.4 ± 3.2% CO_2 evolution respectively in 80 d. Blueberry seeds and walnut shells mineralized more slowly only reaching 39.3 ± 6.9 and 5.1 ± 2.8% CO_2 evolution in 80 d respectively.

1. Introduction

Research on microplastic sources to the aquatic environment has shown that personal care products disposed down the drain are a very small contributor to the overall plastics issue (Duis and Coors, 2016). Even so, many companies that produce personal care products have committed to removing microplastics from their products (Duis and Coors, 2016). Removal of these materials has led to the need to evaluate replacement microparticles for personal care product applications which include naturally occurring materials and biodegradable plastics such as poly(3-hydroxy butyrate)-co-(3-hydroxy valerate), PHBV. However, there are very few relevant test methods available to evaluate the environmental persistence of non-soluble microparticles. Therefore, there is a

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http://dx.doi.org/10.1016/j.chemosphere.2017.02.091
0045-6535/

need to develop new methods or modify existing methods in order to evaluate the biodegradability of non-soluble microparticles. For down the drain disposed materials the route of disposal is well understood. Materials pass through the sewer system and into a wastewater treatment facility. The amount of a material that will be discharged into the receiving environment is dependent on the material's physical and chemical properties as well as its rate of biodegradation and residence time in the sewer and treatment facility. If some of a material leaves a treatment facility, it will either be discharged in effluent thus reaching surface water and sediment, or it will be associated with sludge solids and thus applied to soil, landfilled, or incinerated (OECD, 2008). Based on these well-defined disposal scenarios, a suite of tests (screening through simulation) have been developed to quantify primary and ultimate biodegradability of soluble chemicals in each relevant environmental compartment (ECHA, 2006; OECD, 2006, 2008; USEPA, 2008).

For down the drain disposed chemicals, the OECD 301 Ready Biodegradation series of tests (OECD, 1992) are widely used by scientists and regulators to assess aerobic biodegradability typically using inocula from activated sludge wastewater treatment plants (ECHA, 2006). These tests can be useful as screening tools as they are well prescribed, use indirect measures of biodegradation by following carbon or oxygen, and are relatively inexpensive and easy to perform (Francois et al., 2016). However, the usefulness of these studies is limited due to the conservative nature of the tests. These tests employ high test chemical concentrations and low levels of inocula that are not realistic when compared to actual environmental conditions (Thouand et al., 1996; Goodhead et al., 2014). The low levels of inocula limit the microbial diversity which is unrealistic compared to actual environmental compartments (Struijs and van den Berg, 1995; Goodhead et al., 2014) and also leads to extended time periods needed for the microbes present in the study to adapt to the test chemical as the only food source and for the microbial population to increase to a sufficient level to degrade the high concentration of test chemical (van Ginkel et al., 1995; Itrich et al., 2015; Francois et al., 2016). These conservative test conditions are further confounded by the stringent pass criteria and short test duration (28 d). The pass criteria for an OECD 301 study is defined as 70% removal of dissolved organic carbon or 60% reduction of theoretical oxygen demand or carbon dioxide production for respirometric methods within the 10 d window (beginning at 10% biodegradation) of the 28 d test.

Even with these limitations, the ease of use and relatively inexpensive cost of the OECD 301 test for a screening level assessment has led researchers to investigate extrapolation factors for OECD 301 mineralization rates to actual rates of aerobic mineralization in other compartments (Boethling et al., 1995; Struijs and van den Berg, 1995; Federle et al., 1997). Federle et al. (1997) completed the most comprehensive assessment by comparing mineralization rates for 9 diverse chemicals in an OECD 301B test to realistic ^{14}C-radiolabeled simulation tests using activated sludge, river water, and sludge amended soil. Even though no empirical relationship was found between mineralization rates in the various tests, the research showed that in all cases the OECD 301B test accurately predicted whether or not biodegradation would occur in the other environmental compartments (activated sludge, soil and river water). Additionally, in all cases the mineralization rate from the OECD 301B study was more conservative than the rates of mineralization in the other compartments, further confirming the conservative nature of the test. The OECD 301 Ready Biodegradation Test also has importance from a regulatory point of view, under REACH guidelines a chemical is considered not persistent if it reaches 60% mineralization in 28 d (ECHA, 2012).

PHBV is a thermosplastic polymer synthesized by bacteria which has a variety of applications including packaging, medical implants, and drug delivery (Plackett, 2012). Many forms of PHBV including polymer, films, and foams have been found to be aerobically and anaerobically degraded in a number of environmental compartments including soil, marine and fresh water and sludge (Abou-Zeid et al., 2001; Wing Hong and Yu, 2003; Vá zquez-Rodrígueza et al., 2006; Batista et al., 2010; Plackett, 2012; Deroine et al., 2015). PHBV foam particles are currently being explored for use as exfoliants in personal care products that would be disposed down the drain. The PHBV foam particles can offer different consumer benefits than exfoliants made from naturally occurring materials due to differences in physical properties such as porosity, hardness, and texture to name a few. Although naturally occurring materials such as waxes, nuts, and seeds are commonly used as exfoliants in down the drain disposed personal care products, very little research has been conducted to evaluate the ultimate biodegradability of these natural exfoliants. The only natural exfoliant that has been studied is beeswax. Past research has shown that beeswax is biodegraded rapidly using inocula from oil contaminated soil (Hantsveit, 1992) and activated sludge (de Morsier et al., 1987; Struijs and Stoltenkamp, 1990). Struijs and Stoltenkamp (1990) evaluated beeswax biodegradation using activated sludge inocula and following carbon dioxide (CO_2) evolution and found that beeswax reached 63% evolved CO_2 in 28 d.

The objective of this research was to modify the OECD 301B Ready Biodegradabilty Test as needed in order to quantify the ultimate biodegradability of non-soluble microparticles made of PHBV foam or natural materials including jojoba wax, beeswax, rice bran wax, stearyl stearate, blueberry seeds and walnut shells.

2. Materials and methods

2.1. Overview

This study complied with the OECD 301B Ready Biodegradability Test Guideline (OECD, 1992) which is designed to evaluate the extent of mineralization of a test substance over time by measuring the formation of evolved CO_2. The test substance is the sole carbon and energy source and under aerobic conditions, microorganisms metabolize the test substance producing CO_2 or incorporating the carbon into biomass. This study was conducted using an electrolytic respirometer (Coordinated Environmental Services Ltd., UK). The test apparatus consisted of 1 L bottles that contained the test material, sludge inoculum and mineral media. A conductivity probe immersed in 0.19 M NaOH was used to measure the production of CO_2 and a pressure transducer monitored the decrease in pressure due to oxygen consumption. A sensor assembly charged with 1 M $CuSO_4$ continually equalized the pressure as oxygen was consumed. The test bottles and sensor heads were immersed in a 22 $\pm$ 1.0 °C water bath throughout the study period to precisely control temperature and an automated data logging system continually acquired data at prescribed time intervals.

2.2. Test materials

Sodium benzoate (Alfa Aesar, Haverhill, MA) was used as the positive control and had an organic carbon content of 58.4 $\pm$ 0.10% (total organic carbon, TOC, analyzer, Shimadzu Corporation, Kyoto, Japan). The PHBV polymer used in this experiment was ENMAT Y1000P (CAS no. 1039549-27-3, supplier Tianan Biologic Materials Company, Ltd. Ningbo, China) and was supplied as a pellet that was super-cooled then double milled (100 UPZ Fine Impact Mill, Hosokawa Alpine, Germany) to a fine powder (<32 µm, Hosokawa Micron, UK). The PHBV polymer has a hydroxyvalerate content of 1%, a molecular weight of 485,000 g mol^{-1}, and a polydispersity of