ASSESSMENT OF LEATHER AND LEATHER SUBSTITUTE WASTE BIODEGRADABILITY UNDER AEROBIC CONDITIONS IN LIQUID ENVIRONMENT

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The leather and footwear industry is one of the industries that generate large amounts of leather and leather substitute waste. Waste biodegradation is assessed through tests performed under aerobic conditions in the soil, in an aqueous medium under composting and anaerobic conditions in an organic waste anaerobic digester or under similar conditions in the laboratory. The aim of this paper is to comparatively study biodegradation under aerobic conditions in liquid medium of three types of materials used in the leather and footwear industry, namely: chrome-tanned leather, vegetable-tanned leather and synthetic leather. Biodegradability study was conducted in accordance with EN 13432/02 in a facility for waste biodegradation in liquid medium under aerobic conditions (EN ISO 14852-05). To characterize the biodegradation process, the following were monitored for 100 days: conductivity, total organic carbon content (TOC), total organic nitrogen content (TON) and the degree of waste biodegradation.

Keywords: biodegradation, chrome-tanned leather, vegetable-tanned leather, synthetic leather

INTRODUCTION

The leather and footwear industry is one of the industries that generate large amounts of solid waste, which until recent years have been ignored and huge amounts have been discharged directly into the environment (Zerdan *et al.*, 2004).

Throughout the life cycle, from processing finished leather for shoes, the resulting waste and chemicals contained by some waste can be hazardous to health and to the environment (Stefan *et al.*, 2012b).

In accordance with European legislation, waste from the leather and footwear industry must be exploited by the same methods: reuse, recycling, energy recovery, recovery by chemical and biochemical degradation, recovery of useful organic compounds (Aftab *et al.*, 2006; De Gisi *et al.*, 2009; Dogruel *et al.*, 2004; Mandal *et al.*, 2010; Stefan *et al.*, 2012a; Zaharia *et al.*, 2013).

One way for low-cost recovery of solid waste is biodegradation (Ruggieri *et al.*, 2008).

The aim of this paper is to comparatively study biodegradation under aerobic conditions in liquid medium of three types of materials used in the leather and footwear industry, namely: chrome-tanned leather, vegetable-tanned leather and synthetic leather. Waste pieces are placed in the composting system in a nutrient solution which provides the required C, N, P, Ca and Mg and the inoculum of microorganisms able to biodegrade them. In order to characterize the biodegradation process, the following were monitored: the conductivity and the degree of waste biodegradation by determining the resulting amount of CO_2.

MATERIALS AND METHODS

For the study of biodegradability three types of materials were used, common to the leather and footwear industry, namely: chrome-tanned leather (PCr), vegetable-tanned leather (PTan) and synthetic leather (PS). The biodegradability study was performed according to EN ISO 13432-02: 2002 - Requirements for packaging recoverable through composting and biodegradation - Test scheme and evaluation criteria for the final acceptance of packaging. The facility in which the study was conducted in accordance with EN ISO 14852:1999 - Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by analysis of evolved carbon dioxide, and is shown in Figure 1.

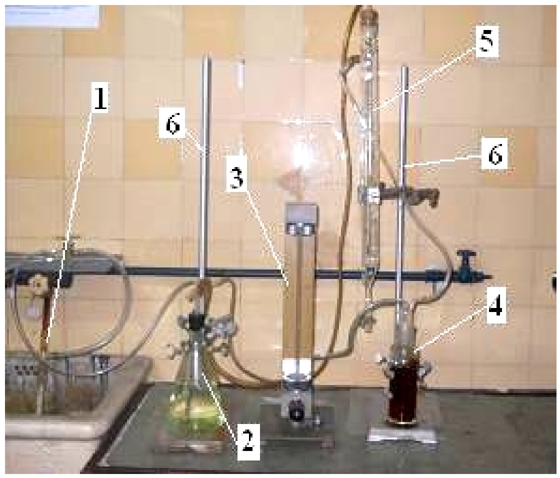

Figure 1. Facility for waste biodegradation in aqueous medium, under aerobic conditions: 1 - vacuum system, 2 - vessel for CO2 absorption from air, 3 - rotameter, 4 - reaction vessel, 5 - CO2 absorption column, 6 – frame.

With the vacuum pump air is circulated through the apparatus, the flow rate measured using the rotameter varies around the value of 2 L/h. The absorption vessel contains 300 mL of KOH in concentration of 10 mol/L and is designed to retain CO_2 from the air. The air free of carbon dioxide enters the reaction vessel which contains about 0.4 g of a waste sample and 250 mL of nutrient solution (prepared from: KH_2PO_4, K_2HPO_4, $Na_2HPO_4*2H_2O$, NH_4Cl, $MgSO_4*7H_2O$, $CaCl_2*2H_2O$, $FeCl_3$*6H2O dissolved in distilled water according to EN ISO 14852-05) and 10 cm^3 of inoculum. The inoculum was prepared from 10 g of compost collected from the biodegradation landfill of leather waste (INCDTP-ICPI) that were put into contact with 100 mL of distilled water. The suspension was stirred for 30 minutes and then filtered; 10 mL of the solution was used as inoculum in the reaction vessel.

In the reaction vessel, degradation processes occur, resulting in carbon dioxide, which is absorbed in the absorption column containing 100 ml of NaOH solution with the concentration of 0.05 mol/L. Carbon dioxide concentration was determined daily by titration with HCl 0.05 mol/L in the presence of phenolphthalein in the first stage and methyl orange in the second step.

In the liquid phase the following were also determined: conductivity, using a conductometer, Jenway 470; total organic carbon content, TOC, using a LiquiCOT analyzer; and total organic nitrogen content, TON, determined by the Kjeldahl method using a Velp Scientifica UDK 130 D apparatus.

The degree of biodegradation was determined using equation 1:

$$R, \% = \frac{Ct}{Ci} \times 100 \qquad (1)$$

where: Ct - the amount of carbon dioxide resulting from the biodegradation facility when the analysis was performed, mg/g; Ci - total organic carbon content corresponding to 1 g of sample, mg/g.

RESULTS AND DISCUSSIONS

Using miocroorganism populations found in the composting landfill of leather waste which were inoculated in a nutrient solution, their degree of biodegradation was monitored. Figures 2, 3, 4 and 5 present variations of conductivity; total organic carbon content, in the liquid phase, TOC; total organic nitrogen content, TON; and the degree of biodegradation. The system was monitored for a period of 100 days.

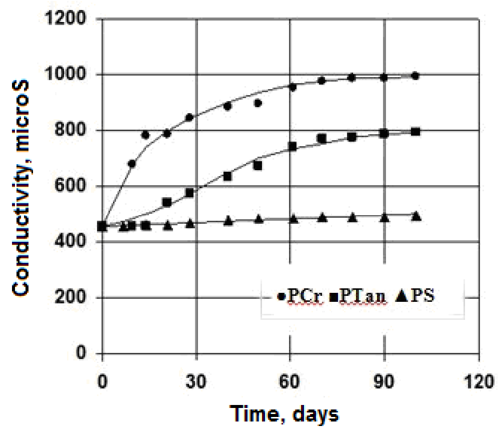

Figure 2. Variation over time of conductivity in the liquid phase

Conductivity in the system increases for all three samples, phenomenon due to salt solubilization and degradation processes that occur.

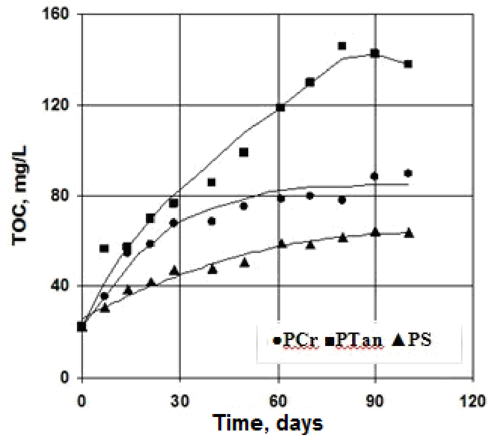

Figure 3. Variation over time of TOC in the liquid phase

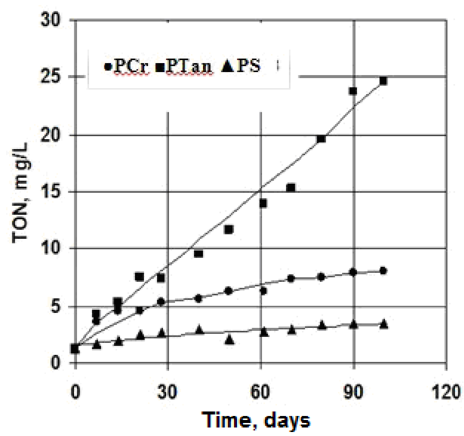

Figure 4. Variation over time of TON in the liquid phase

The increase of total organic carbon and total organic nitrogen concentration in the studied systems prove that degradation processes occur in the system. It is noticed that they are more intense for vegetable-tanned leather waste and much weaker for chrome-tanned leather and synthetic leather.

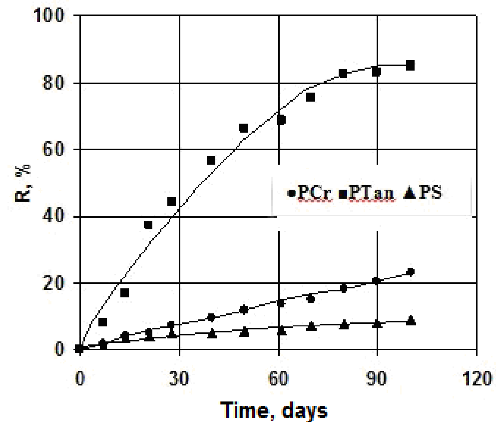

Figure 5. Variation over time of waste biodegradability

Upon analyzing Figure 5, it can be noticed that the degree of biodegradation of vegetable-tanned leather reaches 84% in the 100 days of the study.

The degree of biodegradation of chrome-tanned leather waste and synthetic leather waste reaches 23% and 9%, respectively. Vegetable tanning is a great step towards biodegradation of leather waste; therefore it is recommended to replace the chrome-tanning process with vegetable-tanning, which enables leather waste biodegradation.

CONCLUSIONS

None of the materials subjected to analysis fully complies with the conformity criteria, but vegetable-tanned leather has the closest degree of biodegradation to the required one.

As a result of this study, it was found that vegetable-tanned leather has a biodegradation capacity of 84.6%, chrome-tanned leather of 23%, and synthetic leather of only 9%, which proves that vegetable-tanned leather is biodegradable and comes very close to biodegradability conditions required by EN ISO 13432:2002.

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