Biodegradability of "Eco-friendly" Leather using Respirometric Approach

by

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Abstract

Biodegradability is the ability of degradation of organic substances and materials into more simple inorganic substances through enzymatic activity of microorganisms. The measure of the tanning products biodegradability allows to predict the deterioration of the materials and allows to assess their impact on the environment since chromium, derived from tanning industries, could be transformed in the hexavalent stage of chromium (Cr^{6+}) that is a suspected carcinogen. Three leather samples, have been chosen for biodegradability test, in order to evaluate differences in biodegradability and to evaluate the possibility of using alternative leathers of those based on chromium. It was possible to make a comparison between three different leather samples; among these, the highest percentage of biodegradability was found for the metal- free leather sample (84%) compared to 45% and 80% of the chrome leather and wet-white leather samples. Results highlight the possibility of using differently tanned leathers with a considerably reduced environmental impact.

Introduction

Leather is the material made from animal skin which, following a process called "tanning", is rendered unalterable. Immediately after the slaughter of the animal, the processes of degradation and decomposition of the tissues begin. These processes quickly degrade the quality and value of tissues from the tanning point of view. [1-2] Therefore, it is necessary to start immediately the preservation processes of fresh skins which are useful in blocking skin degradation, for an adequate period of time before the beginning of skin processing, and which include salting, drying and preserving techniques with the cold. These techniques are able to create within the skin those conditions that make life and development of bacteria and microorganisms that produce the enzymes of decomposition, impossible. Preservation is followed by the tanning process that consists of various chemical and mechanical treatments, which make it possible to transform a putrescent organic material (raw skins) into a high value product. Tanned leather cannot be transformed directly into a commercial product, it must undergo further chemical and physical treatments that constitute the finishing phase.

The ecological characterization of commodities has recently become of strategic importance for companies that wish to put on sale finished products with a higher added value. In fact, environmental and ecological problems became a market component, since consumers tend to privilege those goods and services that, from this point of view, are considered more 'eco-friendly'.[3-7] In this context, biodegradability is one of the characteristics that is often taken into account in judging the ecological acceptability of the material, particularly in the phase of its elimination and / or disposal. [8]

Biodegradability is the ability of degradation of organic substances and materials into more simple inorganic substances through enzymatic activity of microorganisms. If the process takes place in presence of oxygen (aerobic process), there is the complete transformation of the organic compound into carbon dioxide and water; in absence of oxygen (anaerobic process), the transformation of the organic compound produces carbon dioxide and methane. In other words, the measure of the tanning products biodegradability allows to predict the deterioration of the materials and, in the context of waste disposal, allows to assess their impact on the environment. [9-11]

Given the tremendous environmental impact determined by the landfill of chromed leather that stays for a long time without observing appreciable levels of degradation, [12-14] it has become

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Manuscript received October 8, 2018, accepted for publication June 6, 2019

necessary to develop a model system to evaluate the biodegradability of leathery materials, even in the light of Regulation 880/92 of the European Union for the assignment of the ecological quality mark of a product throughout its life cycle. Chromium derived from tanning industries could be transformed in water, soil and wastewaters, to the hexavalent stage of chromium Cr^{6+} that is a suspected carcinogen and causes skin sensitization. [15-17] For this purpose, in the last few years alternative tanning systems were proposed, in order to reduce negative environmental impact of chrome. [18-22]

The main purpose of this work is to evaluate the differences in biodegradability among differently tanned skins, in order to state whether the treatments and the tanning products currently used in the industries can produce a biodegradable material. Three leather samples, created by different types of tanning, that are Chromed leather, Leather wet-white and Metal-free organic leather have been chosen for biodegradability test based on respirometric analysis.

Experimental

Materials

The samples examined are bovine leather finished for automotive supplied by an Italian tannery. Leather wet-white is a bovine leather tanned with glutaraldehyde and natural tannins for automotive while Metal-free organic leather is a leather whose content of tanning metals (Cr, Al, Ti, Zr, Fe) does not exceeds 0.1%.

Microscopic and Physic-chemical Analysis

Surface portions of leathers, taken at the rump of the skin, have been analyzed with a stereomicroscope (Optika SZP-10) with a 60X magnification. Section of leathers obtained by cryomicrotome (Bright OTF 5000), with a thickness of 30 μm, have been observed with Optical microscope (Zeiss- Phomi III) at 250 magnification. Chemical parameters were determined in leather samples (Table I). The following parameters were analyzed: humidity and volatile matter, Insoluble ash, Water-soluble Ash, Total Ash, Matter soluble in Dichloromethane, Water-soluble Matter, Dermal substance, pH, Al, Cr, Fe, Ti, Zr, Si and Total metals of leather. All parameters were analyzed according to common international standardized methods. [23-29] Test methods and parameters for the physical determination of leather were listed in Table II. [30-35]

Biodegradability Analysis

The respirometric method provided is based on the determination of CO_2 produced by the material under test when placed in contact with compost, according to ISO 20136-2017. [36] Compost has the function of solid matrix, inoculum of thermophilic microorganisms and source of nutrition. For this purpose, the skins were cut into fragments of about 0.5 cm per side and mixed with the compost. For this analysis, a Spent Mushroom Compost (SMC) of chopped wheaten straw, poultry manure, horse manure and gypsum was used. The mix was maintained at a temperature of 58°C under aerobic conditions and at an appropriate level of humidity, thus trying to simulate typical composting conditions. As the last product of the aerobic biodegradation of the tested material, carbon dioxide, water, mineral salts and new microbial cells that create biomass are produced. The carbon dioxide produced was monitored and recorded at regular intervals, with a frequency of about once every two days, both in the reactor containing the mix and in others that constitute the negative control (consisting only of compost and culture medium). The test lasted 6 months, during which the reactors were incubated in the dark, in a stove at a constant temperature of 58 ± 2°C and injected with carbon dioxide-free air. Air used to aerate composting reactors must be free from carbon dioxide: in order to achieve this result, a trap made up of a sodium or barium hydroxide solution was used. Here the air coming from the peristaltic pump gurgles inside the

Table I
List of chemical parameters analyzed in leather samples.

Parameters	Method
Humidity and Volatile matter (%)	UNI EN ISO 4684
Insoluble ash (800°C) %	UNI EN ISO 4047
Water-soluble Ash (800°C) %	UNI EN ISO 4047
Total Ash (800°C) %	UNI EN ISO 4047
Matter soluble in CH_2Cl_2 %	UNI EN ISO 4048
Water-soluble Matter %	UNI EN ISO 4098
Dermal substance %	ISO 5397
pH	UNI EN ISO 4045
Al (ppm)	UNI EN ISO 17072-2
Cr (ppm)	UNI EN ISO 17072-2
Fe (ppm)	UNI EN ISO 17072-2
Ti (ppm)	UNI EN ISO 17072-2
Zr (ppm)	UNI EN ISO 17072-2
Si (ppm)	UNI EN ISO 17072-2
Total metals of leather (ppm)	-

Table II
List of physical parameters analyzed in leather samples.

Physical parameters	Method
Thickness	UNI EN ISO 2589
Tear load	UNI EN ISO 3377-1
Tensile strength	UNI EN ISO 3376
Percentage Extension	UNI EN ISO 3376
Distension and Strength of Grain	UNI 11308
Shrinkage temperature	UNI EN ISO 3380
Degradation of color with artificial aging to heat and moisture (48h, 55°C, 80% R.H.)	UNI EN ISO 17228 (Method 7D)
Physical effects with Artificial aging to heat and moisture	UNI EN ISO 17228 (Method 7D)
Surface contraction with artificial aging to heat and moisture	UNI EN ISO 17228 (Method 7D)
Degradation of color with artificial aging to heat and moisture (120°C, 7 days)	UNI EN ISO 17228
Physical effects with artificial aging to heat	UNI EN ISO 17228
Surface contraction with artificial aging to heat	UNI EN ISO 17228

solution and, free of CO_2, is introduced in the reactors through a watertight cap. If biodegradation occurs, then carbon dioxide will be produced and it goes out through the pipe that collects the exhausted air, that is directly connected to the carbon dioxide determination system. The resulting carbon dioxide is then absorbed by a trap made up of a barium hydroxide solution, $Ba(OH)_2$, thus obtaining a precipitate of barium carbonate, $BaCO_3$. From the remaining quantity of barium hydroxide, titrated with hydrochloric acid, it was possible to trace the carbon dioxide content.

The following experimental pattern was followed in the study for Chromed leather (A), Leather wet-white (B), and Metal-free organic leather (C):

- Negative control: compost (300g) + culture medium (2 L)
- Positive control: collagen (26g) + compost (300g) + culture medium (2 L)
- Test A: Chromed leather (26g) + compost (300g) + culture medium (2 L)
- Test B: Leather wet-white (26g) + compost (300g) + culture medium (2 L)
- Test C: Metal-free organic leather (26g) + compost (300g) + culture medium (2 L)
- All tests were performed in duplicate and results expressed as average value.

Results and Discussion

Microscopic analysis and organoleptic characteristics of leather samples were reported in Figures 1, 2 and 3. With regard to the structural and product characteristics of the samples examined, the investigations carried out have shown that the chrome-tanned bovine leather is, to the touch, full and soft with a clearly visible and uniform flower design. The other two tanned leathers without the use of chromium salts show an unclear flower design with a softer "hand" (empty wet-white in the sides and organic metal-free tanned by touch). Microscopic analysis of chrome samples have revealed a flower design visible and uniform at the junction area. At the organoleptic analysis the chrome sample showed a full and soft leather. The flower design of wet-white leather, under the microscope, appear to be little obvious but fairly uniform. At the organoleptic analysis the wet-white leather is soft to the touch even if it appears somewhat emptied and swollen in the hips. The metal-free organic leather has a floral design that is unclear and flattened. The results of organoleptic analysis, shown that metal-free organic leather is slightly dry to the touch and at the sides the leather has slight veins and slight wrinkles.

Table III report results of chemical characterization of leather. For both wet-white and metal free organic leathers the quantities of chrome are very low (respectively 179 & 626 ppm). The amount of collagen, expressed as dermal substance to dry weight, is greater for wet-white leather (75.3%). The amount of metals is lower in wet-white leather. The content of collagen for metal-free organic leather is lowest among the samples while the amount of fat extracted with dichloromethane and pH of watery extract is the highest.

Physical determination of the leathers are reported in Table IV. The wet and dry ageing tests on Chromed leather revealed a greater degree of contraction than the other two samples.

In addition, the resistance of the flower to wet-white leather is lower than in chrome and metal-free organic leather. Finally, shrinkage temperature of the leather without chrome (metal free organic leather and wet-white) was found to be, for both cases examined, equal to 82°C, a value somewhat lower than that obtained with chrome tanning.

As far as the chrome leather sample is concerned, Figure 4 shows that the average biodegradation percentage is 45%, which can be reached in approximately 70 days.

For the wet-white leather sample (Figure 5), the average biodegradation percentage is 80%, after about 70 days of monitoring. The metal-free organic leather has biodegradability value after about 70 days, and it is 84% (Figure 6).

If we observe the graphs, we can realize that most of the degradation, especially for chrome leather, takes place within the first two months of incubation. Afterwards, the curve shows a quite constant trend with biodegradation values that do not tend to increase significantly even after six months of incubation.

The values of the chemical and physical tests allow us to affirm that currently, with the alternative chrome tanning systems, it is not possible to achieve the same results, in particular for some parameters such as the resistance of the flower and the shrinking temperature, obtainable instead with conventional chrome tanning. All experimental cases, although at a different time interval, show a kinetic characteristic of biodegradability reaction, that is distinguished by an adaptation time (lag phase) with slow or absent biodegradation, a quite fast phase of exponential biodegradation, and a decrease in speed until reaching a stationary plateau phase, corresponding to the decrease in microbial proliferation due to the exhaustion of nutrients, or rather to the exhaustion of the biodegradable fraction of the handwork.

According to the Standards of Reference (ISO 20136:2017),[36] the test for all three samples can be considered valid since the following requirements are met:

1. The degree of the reference material (collagen) biodegradability is greater than 70% after 50 days;

2. The difference between the biodegradability percentages of the reference material (collagen) in the two reactors is less than 20% at the end of the test;

3. The production of carbon dioxide in the compost after ten days of incubation is between 50 and 150 mg CO_2/g of volatile compound.

The percentage of biodegradation of chrome leather is lower than shown by the other two examined leathers (wet-white and leather with organic tanning). This data requires a deepening; in fact we have examined finished leathers and therefore it is difficult to establish which phase (tanning, retanning, etc.) has a certain influence on the biodegradability of the finished leather.

Despite the minimum quantities of chrome in the wet-white and metal-free samples, in the case of metal-free leather, the simultaneous presence of other tanning metals such as aluminum, means that their sum exceeds 0.1 percent (1000 ppm) which is the limit for the definition of metal-free organic leather required by current legislation (UNI EN 15987:2015).[37] Therefore, the test sample, called metal-free, since it has a tanning metal content of 1633 mg/kg cannot be defined as metal-free.

According to the UNI EN 15987:2015,[34] the most appropriate term for this sample is organic leather, considering that in this case the sum of the tanning metals provides a value lower than or equal to 0.3%.

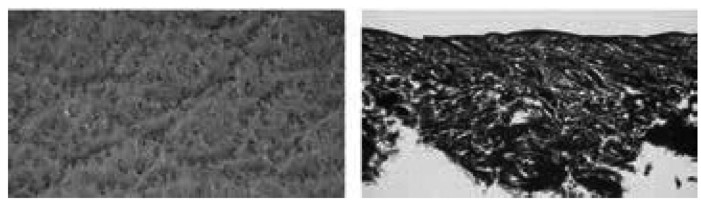

Figure 1. Microscopic analysis of chrome leather. A) View of leather surface, B) View of cross section.

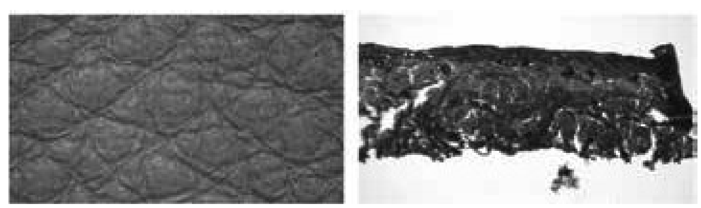

Figure 2. Microscopic analysis of wet-white leather. A) View of leather surface, B) View of cross section.

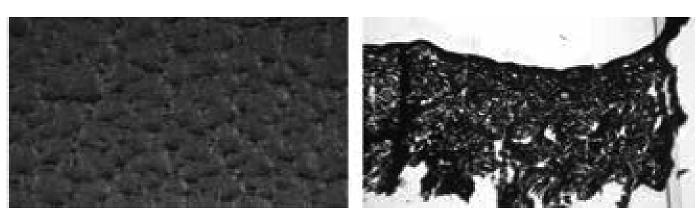

Figure 3. Microscopic analysis of metal free leather. A) View of leather surface, B) View of cross section.

Table III

Results of chemical analysis of leathers.

Parameters	Chrome leather	Wet-white leather	Metal-free leather
Humidity and Volatile matter (%)	8.1	8.0	5.4
Insoluble ash (800°C) %	4.85	0.66	1.08
Water-soluble Ash (800°C) %	0.25	0.44	0.52
Total Ash (800°C) %	5.1	1.1	1.6
Matter soluble in CH_2Cl_2 %	4.4	4.8	7.9
Water-soluble Matter %	0.30	0.92	1.34
Dermal substance %	71.4	75.3	61.9
pH	3.7	4.8	5.1
Al (ppm)	1261	102	755
Cr (ppm)	31822	173	626
Fe (ppm)	286	52	122
Ti (ppm)	25	7	130
Zr (ppm)	-	-	-
Si (ppm)	4766	1456	3281
Total metals of leather (ppm)	33394	334	1633

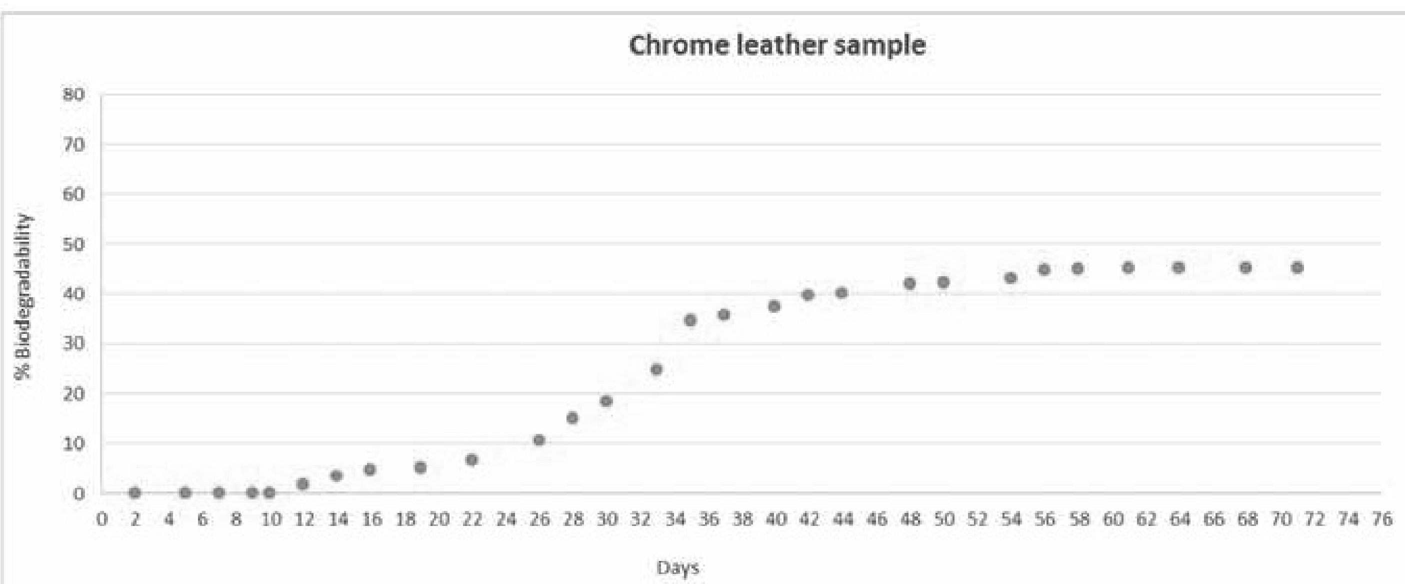

Figure 4. Trend of biodegradability values in Chrome leather sample. On X and Y axes were reported days of measure and biodegradability percentage respectively. Results were expressed as average value.

Table IV

Results of physical analysis of leathers.

Physical parameters	Chrome leather	Wet-white leather	Metal-free leather
Thickness	1.95 mm	1.74 mm	1.63 mm
Tear load	98.7 N	100.5 N	81.5 N
Tensile strength	14.1 N/mm^2	18.8 N/mm^2	17.4 N/mm^2
Percentage Extension	101 %	85 %	87 %
Distension and Strength of Grain	8.9 mm	5.9 mm	7.1 mm
Shrinkage temperature	>100°C	82°C	82°C
Degradation of color with artificial aging to heat and moisture (48h, 55°C, 80% R.H.)	Grade 5	Grade 5	Grade 5
Physical effects with Artificial aging to heat and moisture	None	None	None
Surface contraction with artificial aging to heat and moisture	5.0 %	3.9 %	3.0 %
Degradation of colour with artificial aging to heat and moisture (120°C, 7 days)	Grade 5	Grade 5	Grade 5
Physical effects with artificial aging to heat	None	None	None
Surface contraction with artificial aging to heat	13.0 %	9.8 %	5.7 %

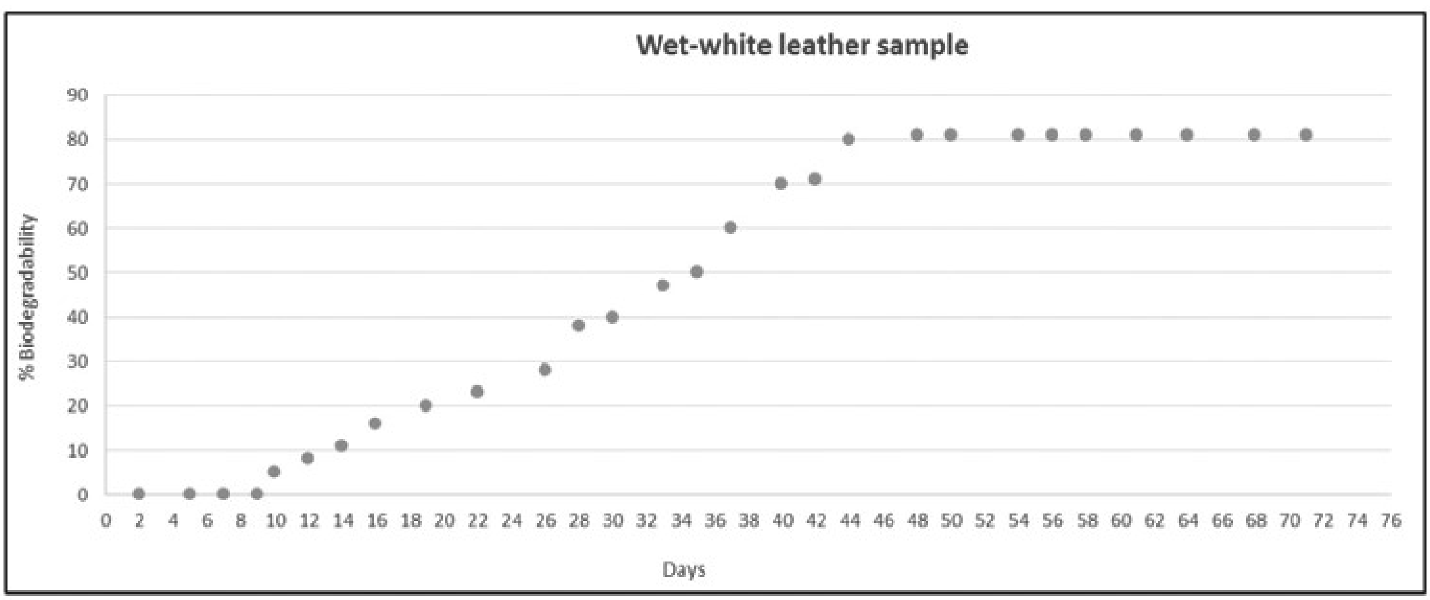

Figure 5. Trend of biodegradability values in Wet-white leather sample. On X and Y axes were reported days of measure and biodegradability percentage respectively. Results were expressed as average value.

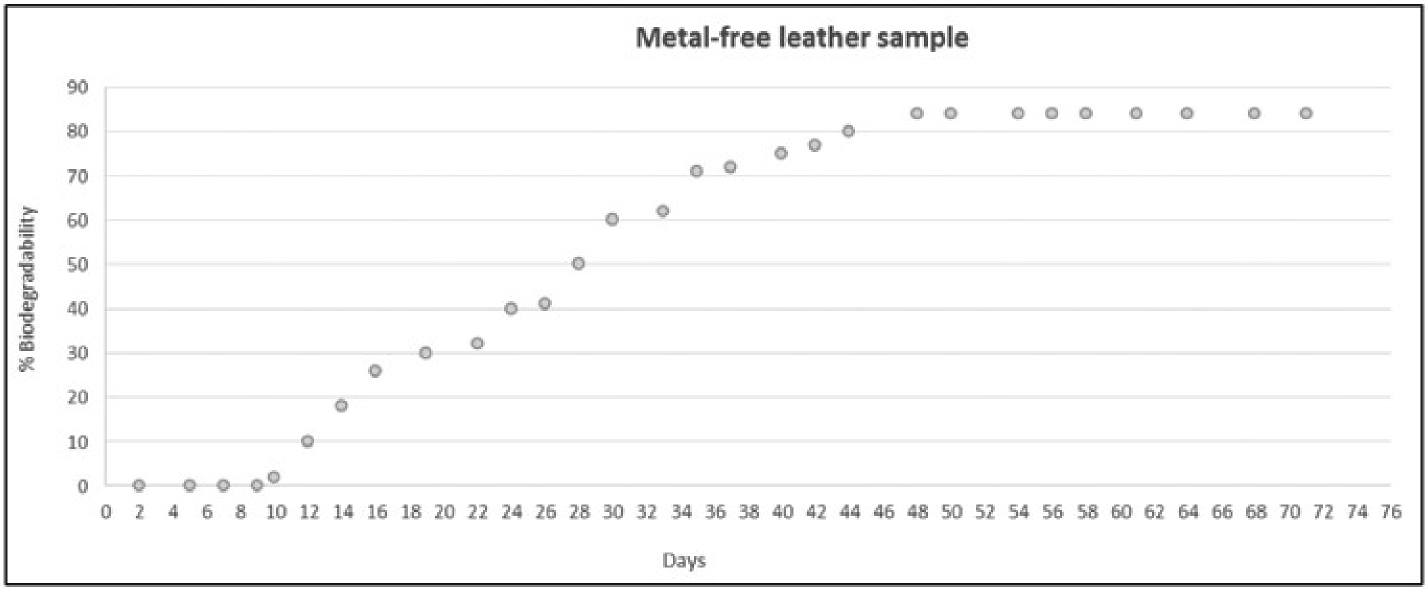

Figure 6. Trend of biodegradability values in Metal-free leather sample. On X and Y axes were reported days of measure and biodegradability percentage respectively. Results were expressed as average value.

Conclusion and Outlook

The methodological approach adopted in this research work essentially focuses on the biodegradability of leathery materials determination, in order to evaluate the possibility of recovering the tested material in composting plants, that is its compostability. Thanks to this methodology we were able to obtain experimental data on leathery materials biodegradability.

In this way it is possible to make a comparison between the different tanning systems and consequently to evaluate the possibility of using alternative treatments of those based on chromium.

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