Retanning Bioagent Used in Leather Processing and Process of Obtaining Thereof

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Currently, the leather industry has to deal with very high costs for waste treatment and disposal. As a result, it is recommended to subject the organic protein waste from tanning to biochemical treatments for recycling in the industry. The degree of novelty lies primarily in the fact that the starting point of the promoted technologies is obtaining new complex products by processing organic waste and using it in tanneries. The lime fleshings resulting from the hide fleshing operation represents the highest amount of reusable leather material of approx. 25%. This paper presents an innovative process for the biochemical degradation of hide waste resulting from hide fleshing in order to obtain a retanning/filling agent used in leather processing.

Keywords: hide waste (fleshings), retanning/filling agent , recycling

Leather industry generates huge amount of fleshing waste, which is rich in proteins and lipids that have potential for various applications [1-3]. From every ton of hide about 100 kg of fleshing waste is engendered accounting to the production of 700,000 tons of fleshings worldwide every year. Fleshings are considered as hazardous due to content of sodium sulfide, a corrosive and an asphyxiating chemical and need to be disposed of securely [4]. Therefore, it is essential to utilize the waste for preparation of various value added products thereby making the environment clean. The protein part of fleshings has been utilized for various applications [5,6]. The lipid content of tannery fleshing waste is remarkable and suitable methods have not been reported for the recovery of lipids.

The non-edible and low cost lipids could be used as a feedstock for biodiesel production [7] and the lipids could be extracted from biomass using Bligh and Dyer, Folch and Soxhlet extraction methods [8]. The extraction efficiency could be improved by disrupting the biomass prior to extraction by autoclaving, sonication, micro-wave irradiation, surfactants and enzymes [9]. Therefore, a viable tissue disruption method is essential for optimal recovery of lipids from fleshing waste, in order to develop a green and cost effective[10].

All waste treatments are mainly aimed at substantially reducing environmental pollution. For this purpose, unprocessed hide waste (fleshings, pelt splits and trimmings, as well as protein from the ash exhaust solution) is best suited for processing into protein form with different degrees of denaturation and purity.

Current technologies are primarily intended for untanned hide waste [11] and generally aim to extract the collagen protein, the basic leather component, in the form of short fibers or dissolved, for the highest yield that can be used as a protein binder, such as a source of collagen in the pharmaceutical and cosmetic industry, the footwear industry in manufacturing insoles obtained from tanned (chrome) leather, or for the production of fertilizers[12].

This paper presents an innovative process for the biochemical degradation of hide waste resulting from hide fleshing in order to obtain a retanning/filling agent used in leather processing, which was characterization by chemical and FT-IR Analysis.

Experimental part

Materials

Untanned waste (fleshing) was obtained from SC Pielorex Jilava, Ilfov County, and were kept at room temperature and analyzed to determine *p*H, humidity, ash, total Kjeldahl nitrogen (TKN) using standardized methods. Moisture was determined by heating the sample at 110°C for 12 hours. Ash from dry products was determined by heating the sample at 600°C for 3-6 hours. TKN was determined by the semi-micro Kjeldahl method.

The chemical characteristics of hide waste (fleshings) used in experiments are presented in Table 1.

Obtaining of hydrolysate

The proposed procedure for the valorization of hide waste (fleshings) into high added value by-products is the following: 1500 g of hide waste (fleshings) are weighed and washed with running water at a temperature of 20-30°C in a drum, for 2-3,5 hours and decalcified with 1.5-3.5% ammonium sulfate for 2-3.5 hours; waste is shredded with a TC 32 grinder (double knife) from SAP-Italy. Hydrolysis occurs in two stages: the first stage is done at a temperature of 35-40°C with the addition of concentrated proteolytic enzyme product containing 30,000 units/g of lipase; 900 units/g cellulase; 1,200 units/g amylase and 10,000 units/g protease for 1.7-3.5 hours, then temperature is raised to 85-100°C and 0.9-1.2% H_2SO_4 is added continuous, for 1-2.5 hours.

Biochemical treatment consists in processing hide waste (fleshings) with a set of enzymes, coenzymes and natural improvers with *starter* fluids, which modify the toxic reactions of the protein hydrolysate with a corresponding elimination of hydrogen sulphide, mercaptans, ammoniacal odours and other specific odours. The product used is commercially known as Dekosinth and is produced in Switzerland.

Obtaining of Retanning Agent

In order to obtain the leather retanning/filling agent, complexing agents (dicarboxylic acids, metal oxides based on titanium or sodium tripolyphosphate) are introduced into the collagen matrix. This filler compared to other similar products has the advantage of eliminating some additional technological operations in the retanning process (salt

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No.	Characteristics,	UM	Determined values	Test method standard number
1.	Dermal substance	%	20-25	SRENISO 4684-2006
2.	Ash	%	15-18	SRENISO 4047-2002
3.	Total nitrogen	%	14.64	SRISO 5397-96
4.	Volatile matter, %	%	82-85	SRISO 5397-96
5.	pH of aqueous extract	%	12	STAS 8619/3-1990

Table 1
CHEMICAL CHARACTERISTICS OF HIDE WASTE (FLESHINGS)

No.	Characteristics,	UM	Determined values	Test method standard number
1.	Dermal substance	%	20-25	SRENISO 4684-2006
2.	Ash	%	10-15	SRENISO 4047-2002
3.	Total nitrogen	%	15.7	SRISO 5397-96
4.	Volatile matter, %	%	85-90	SRISO 5397-96
5.	pH of aqueous extract	%	5-5.5	STAS 8619/3-1990

Table 2
PHYSICAL-CHEMICAL CHARACTERISTICS OF THE RETANNING/FILLING AGENT OBTAINED

purification), therefore it presents an economical advantage and is a natural biopolymer based on collagen, it is ecologic (formaldehyde-, phenol- and chromium-free), and it is suitable for making a wide range of leather assortments. Forwards, in order to obtain the leather retanning/filling agent, a solution of 0.1-0.5% NN' Methylenebis (acrylamide) dicarboxylic polymer, used in the field of foil and synthetic fibers, is introduced into the collagen matrix and the value *p*H to 5-5.5 with a weak triethanolamine-based organic baseline, and stirring is continued for 60 minutes at 90°C. The resulting composition is concentrated by boiling under normal pressure or under vacuum until the concentration exceeds 20-25%. is filtered out of the reaction vessel, having a protein content of about 85-90%, ash 10-15%, dry substance 20-25%, and pH of the solution 5-5.5.

Results and discussions

The retanning agent obtained according to the framework technological process was analyzed physico-chemically with the following characteristics (Table 2):

IR spectra were measured with a range of 7800-350 cm^{-1}; optical system - monobeam; resolution 0.2-16 cm^{-1}; that can measure spectra in transmission, reflection and absorption. Infrared Spectroscopy (IR) is the most appropriate method of identifying the presence of polar functional groups in the structure of molecules of organic compounds. Depending on the wave number, the bands can be assigned to the specific functional groups of finishing compounds and collagen processed in tanneries (Figure 1).

According to spectral assignments, the bands corresponding to the amide groups ($\nu_{C=0}$ at 1636cm^{-1}, δ_{NH} and ν_{C-N} at 1549cm^{-1}) were observed for the retanning agent. Also, signals characteristic of NH groups are present at 1345 cm^{-1}. The OH groups in the hydroxyproline units give a signal at 1081 cm^{-1}. The amide absorption band II is given by N-H deformation and C-N stretching modes. The absorption bands for amide III are attributed to several stretching vibrations: C-N and C-O but also deformation vibrations: N-H and O=C-N.

Application of retanning bioagent for wet finishing of leather

The bovine animals processed up to the pickling stage including, according to known procedures, are pre-slaughtered in a tambour barrel at a speed of 7-10 revolutions per minute. Parameters of the pickl float are: 40% fleet ratio, temperature 20-25 °C, *p*H 2.9 units, density 1.055 g / mL. In this fleet, 10% of the tanning composition obtained, based on the weight of the gelatin skin, is dosed, when the *p*H of the pretancing fleece decreases to about 1.8 units. After 120 minutes of stirring, the penetration of the tanning composition into the skin is controlled, and then 1.5% of the precursor agent and the stocking agent, and 1.5-2.0% of the magnesium oxide (or commercial autobascination agent, containing magnesium oxide) to

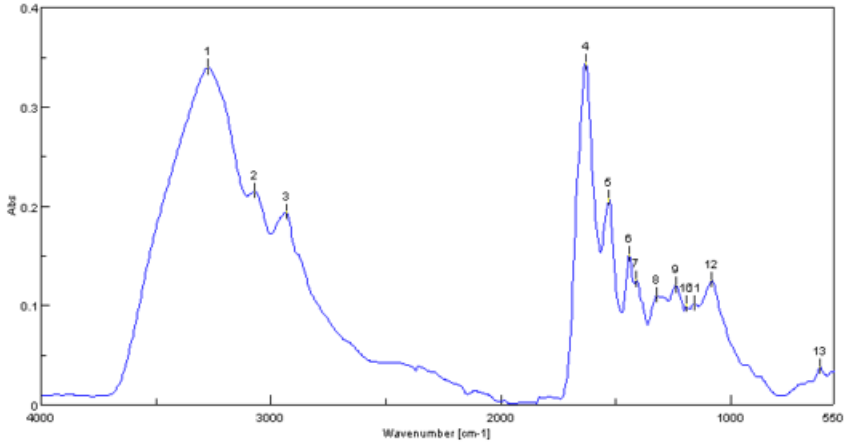

Fig. 1. FT-IR spectrum for tanned agent

fix the tan in the dermis section. Stirring continues for 360 minutes. At the end of the pre-bagging operation, the fleet's pH reaches 3.5 units.

The pre-fabricated leather products thus acquire a shrinkage temperature of 72°C, sufficient to maintain dimensional stability during subsequent mechanical operations. Further, the skins can be processed and finished according to any known technological variants.

Conclusions

The advantages of the retanning bioagent:

- the composition is obtained by a relatively simple and inexpensive process;
- Bio-product with high value added;
- the use of the retouching composition does not require the modification of the current leather processing technologies;
- the composition has a reduced eco-toxicity and contributes to maintaining the health of the people and the environment;
- leads to a reduction in the costs of tanning with the storage and / or transport of solid waste.

The grain of the semi processed leather is smooth and the color is almost white. The resulting leather is filled with an apparent increase in volume, making it comparable to the wet-white leathers produced by classical technologies. The protein content of the pretanned leather is 81%, the metal oxides content is 7%, the total mineral substances are 11%, the pH of the aqueous extract is 3.6 and the volatile content is about 13% .

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation UEFISCDI, Project number PN-III-P2-2.1-CI-2018, Contract number 249/ 2018.

References

1 CONSTANTINESCU, R.R., CRUDU, M., ZAINESCU, G., COARA, G., Rev. Chim. (Bucharest), **66**, no.8, 2015, p.1244-1246.
2.PANTAZI, M., STEFAN,D.S., CONSTANTINESCU, R., ANGHEL, R., MEGHEA, A., VASILESCU, A.M., Rev. Chim. (Bucharest) **65**, no. 2, 2014,p 233-236,
3.KAMINI, N.R. et al., Curr Sci, **77**, 1999, p. 80-86.
4.SARAVANAN, P. et al. J Clean Prod, **79,** 2014, p. 258-264, https://doi.org/10.1016/j.jclepro.2014.05.022.
5. KUMAR, A.G. et al. Bioresource Technology, **99**, 2008, p. 1935–1939.
6. RENITHA, T.S. et al.), Rsc Adv, **5,** 2015 p. 9891-9897, https://doi.org/10.1039/C4RA13811B.
7.BALA, D.D. et al., J Clean Prod, **104**, 2015, p.273-281, https://doi.org/10.1016/j.jclepro.2015.05.035.
8.AZĂINESCU, G.A., CONSTANTINESCU, R.R., VOICU, P., DESELNICU, D.C., Rev. Chim. (Bucharest), **67**, no.1/2016
9. LAI, Y.S. et al., Green Chem, **18**, 2016, p.1319-1326, https://doi.org/10.1039/C5GC02159F.
10. DANG, Y. ET AL., Waste Manag, **52**, 2016, p.360-366, https://doi.org/10.1016/j.wasman.2016.03.054.
11. CHRISTIE, W.W. W.W. (Ed.), Lipid Analysis: Isolation, Separation and Structural Analysis of Lipids, J. Barnes and Associates, 2003, p.205-225.
12. ZAINESCU G., , CONSTANTINESCUR.R., ALBU L., Rev. Chim. (Bucharest) **69** no. 1, 2018, p. 101-104

Manuscript received: 29.11.2018