BIOTECHNOLOGY FOR OBTAINING A RETANNING AGENT FROM FLESHINGS

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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. 15%. 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.

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

INTRODUCTION

Leather industry generates huge amount of fleshing waste, which is rich in proteins and lipids that have potential for various applications (Kamini *et al.*, 1999). From every ton of hide about 10 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 (Saravanan *et al.*, 2014). 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 (Kumar *et al.*, 2008; Renitha *et al.*, 2015). 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 (Bala *et al.*, 2015; Bokhari *et al.*, 2016) and the lipids could be extracted from biomass using Bligh and Dyer [B & D], Folch and Soxhlet extraction methods (Perez-Palacios *et al.*, 2008). The extraction efficiency could be improved by disrupting the biomass prior to extraction by autoclaving, sonication, micro-wave irradiation, surfactants and enzymes (Lai *et al.*, 2016). 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.

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 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.

Following the hydrolysis of fleshings, the surface fat will be separated by the steam and will be sold as a byproduct for processing into soap or biodiesel.

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 pH, 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 4 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.

Table 1. Chemical characteristics of hide waste (fleshings)

No.	Characteristics / UM	Determined values	*uncertainty	Method standard
1.	Volatile matter, %	89.30	± 0,42	SRENISO 4648-2006
2.	Ash, %	12.52	±0,27	SRENISO 4047-2002
3.	Total nitrogen, %	10.93	±0,66	SR ISO 5397-1996
4.	Dermal substance, %	61.43	±2,26	SR ISO 5397-1996
5.	pH of aqueous extract	9.00	±0,10	SRENISO 4045-2008
6.	Fatty substances, %	41.59		STAS 145/20-1988
7.	Metal oxides, %	12.52		ICPI method

Obtaining of hydrolysate

The proposed procedure for the valorization of hide waste (fleshings) into high added value by-products is the following: 5 kg of hide waste (fleshings) are weighed and washed with running water at a temperature of 20-25°C in a drum, for 1-3 hours and decalcified with 2.5-3.5% 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 1.8-3.5 hours, then temperature is raised to 90-100°C and 1-1.3% H₂SO₄ is added continuous. The hydrolysate preparation equipment is shown in Figure 1.

Figure 1. Hydrolysis equipment (grinder for pelt waste and autoclave)

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 Dekosin[®] 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 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.

These leather wastes were treated by chemical-enzymatic hydrolysis. Thus, a quantity of hide waste (fleshings), then mixed with water (50%) and hydrochloric acid in concentration of 6...8% for 4-6 h. The mixture is hydrolysed in a 50 l autoclave with double jacket and stirrer, adding dicarboxylic acids in concentration 0,8-1% at a temperature of 90-98°C for 1 hour.

RESULTS AND DISCUSSIONS

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

Table 2. Physical-chemical characteristics of the retanning/filling agent obtained

No.	Characteristics, UM	Determined values	Test method standard number
1.	Volatile matter, %	84,04	SR EN ISO 4684 -2006
2.	Extractible substances, %	undetectable	SRENISO 4048 - 2008
3.	Total ash, %	9,41	SR EN ISO 4047 - 2002
4.	Total nitrogen, %	7,58	SR ISO 5397-1996
5.	Dermal substance, %	42,61	SR ISO 5397 - 1996
6.	Metal oxides	5,41	ICPI method
7.	pH of aqueous extract	3,5	SRENISO 4045 -2008

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 2).

Figure 2. FT-IR spectrum for tanned agent

According to spectral assignments, the bands corresponding to the amide groups ($\nu_{\text{C=O}}$ at 1636cm^{-1} , δ_{NH} and $\nu_{\text{C-N}}$ at 1549cm^{-1}) were observed for the retanning agent. Also, signals characteristic of NH groups are present at 1345cm^{-1} . The OH groups in the hydroxyproline units give a signal at 1081cm^{-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.

CONCLUSIONS

The paper presents a biotechnology for obtaining a retanning agent from hide fleshings. The composition presented in the paper is obtained by the biochemical degradation of hide waste from leather tanning in order to make a retanning/filling agent which will provide leather with the following characteristics: increased wear resistance, reduced water absorption, softness, greater or less flexibility depending on the assortment.

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.

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