

# Obtaining New Biocomposite Used As Nutritional Substrates

RODICA ROXANA CONSTANTINESCU<sup>1,2</sup>, MARIAN CRUDU<sup>1\*</sup>, GABRIEL ZAINESCU<sup>1</sup>, GHEORGHE COARA<sup>1</sup>

<sup>1</sup>National R&D Institute for Textile and Leather – Division Leather and Footwear Research Institute, 93 Ion Minulescu Str., 031215, Bucharest, Romania

<sup>2</sup>University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1 Polizu Str., 011061, Bucharest, Romania

*Leather industry produces a considerable amount of solid and liquid waste, which raises serious problems in terms of its environmental impact. These waste disposal problems are an obstacle for the industry, and therefore there is the need for alternative methods of converting waste into various products - biocomposites - and their use as a fertilizer, nutritional substrates for plants. This paper presents the development of nutritional substrates with protein biocomposites from pelt waste using an experimental installation for manufacturing biodegradable nutritional substrates. All samples (leather waste and protein biocomposites) were characterized by modern instrumental analyses. Work results suggest the capacity to transform industrial waste into a value-added product for soil rehabilitation.*

**Keywords:** leather waste, biocomposites, nutritional substrate

The problem of waste as a whole is not a simple one, requiring a comprehensive approach in all aspects, ranging from management - identification and inventory, to proper treatment for annihilation, recycling, reuse, which implies concern, financial and technological support, and last but not least, the existence of an adequate legal, institutional and administrative framework (1-3). All the treatments applied to untreated waste were aimed primarily at substantially reducing environmental pollution. For this purpose, rawhide waste (pelt fleshings, splits and trimmings and proteins from the solution exhausted from the liming operation) are the most suitable for processing in the form of protein, with varying degrees of denaturation and purity (4). Research for rawhide waste recovery is directed towards obtaining protein composites by biochemical treatment with microorganisms/enzymes and obtaining hydrolysed proteins and nutritional substrates with various uses (5-7).

Using biocomposites by compounding collagen hydrolysates from pelt waste with various biodegradable polymers stimulates enzymatic substances in the plant, favours the development of the root system and increases the ability of seed germination, favouring the development of rootlets (8-10). All samples (leather waste and protein biocomposites) were characterized by modern instrumental analyses.

Application of innovative biotechnologies for pelt waste recovery leads to the development of biodegradable nutritional substrates. The advantages of using these nutritional substrates arise from the fact that, compared to currently used plastic substrates, the former are biodegradable, having protein biopolymers in their composition (10-14). Biocomposites can be varied depending on the vegetative stages of plants and the type of cultures, being able to correct nutritional and soil nutrient compounds deficiencies (due to technological or climatic stress factors (15, 16)).

## Experimental part

### Materials and methods

In this paper, we used pelt waste (weighing 3 kg) from SC Pielorex Jilava tannery, Ilfov county. Raw hides include, based on the dry weight, 50-68% protein, 0.6-9% fat, 15-50% ash, and less than 5% water. The paper proposes a treatment technology by hydrolysis of pelt waste in acidic medium. Pelt waste is ground with a C/E 660 grinder (double knives), yielding a pasty homogeneous mass - protein biopolymer, then followed by the actual hydrolysis in double jacketed 50l autoclave adding 3%  $K_2HPO_4$ , 1% B and 3-5% HCl at 90-98°C for 2.5-5 h. This protein biopolymer can be used as nutritional substrate for plants (fig. 1).

### Obtaining biocomposites from rawhide waste (pelt)

By combining the biopolymer with various natural and/or synthetic polymers (polyacrylamide, latex, corn starch, etc.), biocomposites are obtained which can be used in agriculture as fertilizer for soils, particularly degraded ones, or they can be used to make biodegradable nutritional substrates for plants. Organic biopolymers are a source of raw materials for agriculture, as protein waste composition provides sufficient elements to improve the composition and help remediate degraded soils, while plants can use some of the elements: nitrogen, magnesium, sodium, potassium, etc.).

Composition of biofertilizers consists in:

- protein hydrolysate obtained from pelt waste mixed with different soils (clay, peat). The type of soil must ensure a controlled porosity in the substrate structure so that the physico-chemical processes of mineralization and contact with soil would lead to adjusting the length of biodegradability;
- auxiliaries with the role of regulating biodegradation capacity of the nutritional substrate, controlling mechanical

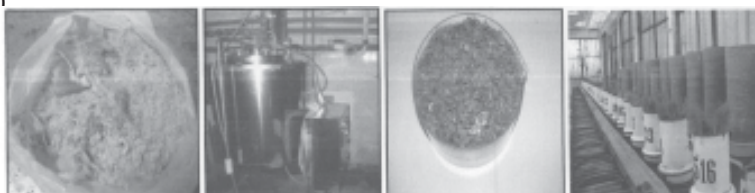


Fig. 1. Technological process for obtaining the protein biopolymer

\* Tel.: (+40) 0722612025



Fig. 2. Experimental installation for obtaining nutritional substrates

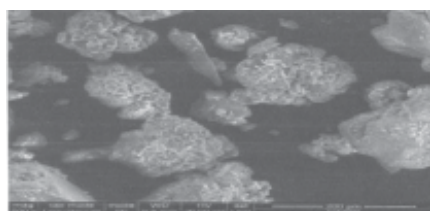


Fig. 3a. Micrograph for sample 2, zoom 500x

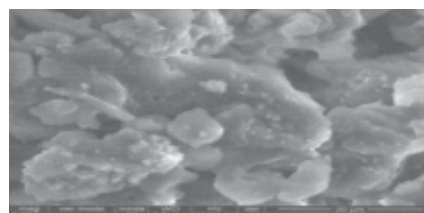


Fig. 3b. Micrograph for sample 2, zoom 5000x

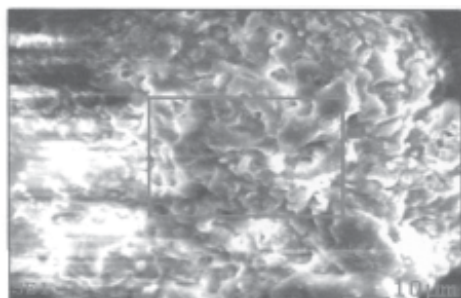


Fig.4a. Surface of the analysed sample

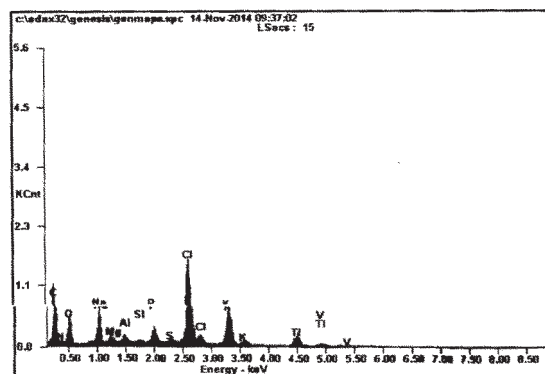


Fig.4b. EDAX elemental analysis of polymeric product for soil remediation

strength, establishing an optimal balance of nutrients and ensuring plant prophylaxis.

The obtained biocomposite can be used in the garden as soil improver and as a fertilizer. In addition, it can be used as an additive and natural fertilizer for plants. In light and sandy soils the biopolymer increases the water retention capacity and nutrient fixation. In hard and clayish soils the biopolymer improves soil structure. The biocomposite contains all essential nutrients and trace elements necessary for plant growth.

#### *Developing the installation for obtaining nutritional substrates*

Developing an installation for biodegradable composites using a mold was one of the main objectives of this work (fig. 2).

The conditions for constructing the mold for nutritional substrates were analyzed in correlation with environmental conditions of plant growth and development.

The advantages of using these nutritional substrates arise from the fact that, compared to currently used plastic substrates, they are biodegradable, having protein biopolymers in their composition. Biodegradable nutritional substrates belong to a new generation of culture media and are designed to meet two distinct functions:

- support for seedlings for a variable period of time, depending on the plant cultivated;
- biologically active material, which gradually degrades in the soil, providing it with biostimulating effects.

#### **Results and discussions**

Research has shown that the hydrolysis of protein waste can lead to new, state-of-the-art organo-mineral protein fertilizers, with the mission of potentiating transport of nutrients to and in the plant, resulting in stimulation of metabolism, speeding the productive phase, stimulation of self-defense system of the plant and optimization of mechanisms responsible for the health of the fruit.

The composition of nutritional substrates consists of:

- protein hydrolyzate obtained from pelt waste mixed with different soils (clay, peat). The type of soil must ensure a controlled porosity in the substrate structure so that the

physico-chemical processes of mineralization and contact with soil would lead to adjusting the length of biodegradability;

- auxiliaries with the role of regulating biodegradation capacity of the nutritional substrate, controlling mechanical strength, establishing an optimal balance of nutrients and ensuring plant prophylaxis.

Characterisation of the sample of polymeric product for soil remediation

SEM micrographs of the polymeric product for soil remediation are presented in figures 3a-3b.

Micrographs reflect the granular and uneven structure of the studied sample with particles smaller than 500mm. This structure is visible for all magnifications used.

Results of sample surface microanalysis are shown in figures 4a and 4b.

The FTIR spectrum of the polymeric product for soil remediation is shown in figure 5.

As figure 5 shows, in the FTIR spectrum of the analysed polymeric product, all bands specific to the matrix of the collagen polypeptide can be identified, such as those at 1658  $\text{cm}^{-1}$  and 1541  $\text{cm}^{-1}$  (amide I and amide II bands, respectively), as well as those at 3406  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$  specific to C-N bonds. Bands at 2930 and 2876  $\text{cm}^{-1}$  probably characterize asymmetric and symmetric vibrations of  $\text{CH}_3$  and  $\text{CH}_2$  groups.

#### **Thermogravimetric analysis**

Figures 6a and 6b present TG and DTG curves of the polymeric product used for soil remediation, recorded at the heating rate of 10°C min<sup>-1</sup>, in inert atmosphere (nitrogen).

Biocomposite composition:

- Organic substances: 38-83%;
- NPK 11-5-8;
- pH = 3.8-7.9

Method of application: The water-soluble product is applied in the soil or by means of the irrigation system by

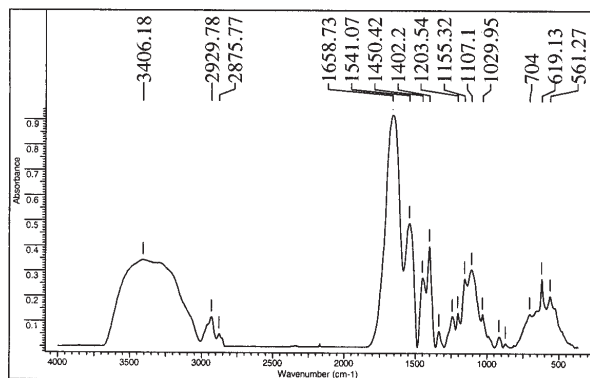


Fig. 5. FTIR-ATR spectrum of the polymeric product used for soil remediation

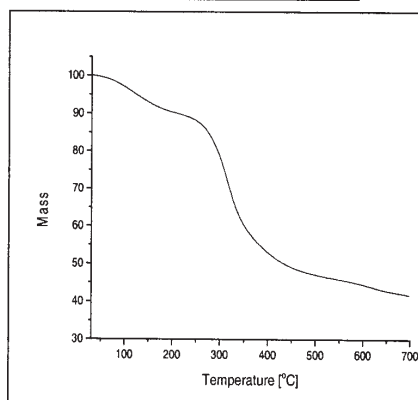


Fig. 6a. TG curve of the polymeric product used for soil remediation

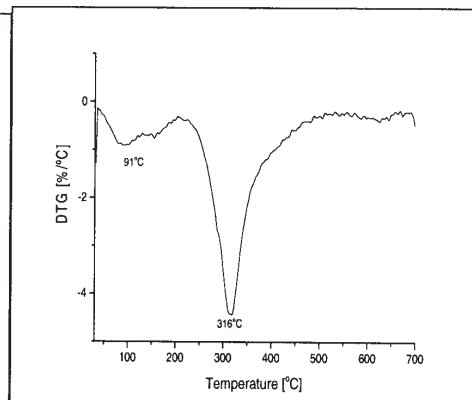


Fig. 6b. DTG curve specific to the polymeric product used for soil remediation

dripping or by foliar application. When applying by dripping, overirrigation is to be avoided, so that the product stays in the area of action of the root system, from where it can be absorbed by plants under optimal conditions.

Recommended dose and uses: 25-30 kg/ha, applied several times during vegetation period for all cultures, on degraded soils.

## Conclusions

The developed technology provides an ecologic and cost effective solution for protein waste recovery from the leather industry in the form of composite materials that can be used in the production of biodegradable nutritional substrates.

Biodegradable nutritional substrates based on protein biocomposites from leather waste and peat, with additional protective and stimulating materials, are a superior form of transport used in current technologies for producing seedlings of plants; therefore these nutritional substrates have the following advantages:

- they are biodegradable, as they are made of natural compounds;
- they completely degrade physically during a life cycle of plants transplanted into the soil;
- they allow direct transfer of plants into the soil without disturbing the roots;
- when using this form of transplant no solid waste is generated, as in the case of using plastic or ceramic substrates;
- they have good permeability to water and air;
- due to their porous structure, they increase the capacity of plant roots to penetrate walls
- they are biodegradable and contribute to soil bioremediation.

*Acknowledgements: The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398*

## References

1. G. ZAINESCU, D. C. DESELCU, I. IOANNIDIS, R. CONSTANTINESCU, C. SIRBU, J. of Int. Sci P- Ecology&Safety, V 7, Bulgaria, 2013, pp 345-352
2. ZAINESCU, G., ALBU, L., VOICU, P., SANDRU L., ALBU E., Int. Conf. on Soil-Water Systems - ConSoil 2008 Milano - Italia.
3. ZAINESCU, G., VOICU, P., ALBU, E., SANDRU L., Patent request no. A 00655, Romania, (2008),
4. CIOBOTARU, V., VIŞAN, S. I. Conf. "Management of Technological Change", Chania, Greece, 2003.
5. L. ALBU, V. DESELCU; Editura CERTEX, 2007
6. A. GAMMOUN, S. TAHIRI, A. Albizane et al., Journal of Hazardous Materials, 2007, vol. 145, no. 1-2, p. 148-153.
7. KURIAN JOSEPH, N. NITHYA, J. of Cleaner Production, 17 (2009) 676-682
8. DIX J.P., Chemical developments leading to cleaner production, World Leather, may 2000
9. THANIKAVELAN P., SARAVANABHAVAN S., RAO J. R., CHANDRASEKARAN B., NAIR B. U., RAMASAMI T., Applied for Indian and PCT Patent CSIR Ref. No. NF425/04, 2004.
10. CHIRIŢĂ G., CHIRIŢĂ M., Chimia Pielii, Ins. Politehnic Iasi, Editura Didactică şi Pedagogică (1987), pg. 15-23
11. ZAINESCU G., P. VOICU, E. BARNA, CERTEX Pub. ISBN 9-789731-716572, 2009, p 46-60
12. V. FERNÁNDEZ, T. SOTIROPOULOS, P. BROWN, I (IFA), France, 2013, ISBN 979-10-92366-00-6
13. E. HERNÁNDEZ-BALADA, M. M. TAYLOR, J. G. PHILLIPS, W. N. MARMER, E. M. BROWN, Bioresource Technology V. 100, I 14, July 2009 p. 3638-3643.
14. Kurian Joseph, N. Nithya -Journal of Cleaner Production, 17 (2009) 676-682
15. \*\*\* International Union of Leather Technologists and Chemists Societies (IULTCS), IU (IUE). 2004., UK: IULTCS. Available at <http://www.iultcs.org/environment.asp>
16. CRUDU, M., SIBIESCU, D., GURAU, D., CONSTANTINESCU, R. R., VASILESCU, A. M., Rev. Chim. (Bucharest), **66**, no.7, 2015, p. 958

Manuscript received: 3.12.2104