SMART BIOPOLYMERS FROM PROTEIN WASTES USED IN AGRICULTURE

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The area of interest is the synthesis and study of properties of new types of hydrogels made from pelt waste, in order to recover waste from tanneries. The complex aspects related to protein projects in the leather industry are addressed by accurately determining a chemical composition, a skin designer and a different possibility of recovery and claiming a value, the use of biotechnology. The complex aspects related to protein waste in the leather industry are addressed by accurately determining the chemical composition of leather waste and the different possibilities of recovery and recycling using biotechnology. The technologies used in order to obtain a smart hydrogel based on collagen and natural polymers are non-polluting and waste-free. An important aspect to note is that the smart hydrogel is obtained through an almost identical technological process to the one used for medical collagen. An extensive study of the potential for reuse and recycling of leather protein waste in ecological conditions by developing innovative procedures for obtaining an NPK collagen matrix to be used successfully as smart fertilizer for modifying nutrient-poor soils. Hydrogels with collagen structure are characterized by a high-performance instrumental analysis system (FT-IR-ATR, SEM, EDAX, etc.).

Keywords: pelt waste, collagen hydrolysate, smart fertilizers

INTRODUCTION

Leather is one of the important sectors globally, nonetheless, the process of conversion of raw hides or skins into non-putrescible leather involves usage of large volume of water, chemicals and mechanical processes to remove unwanted components so as to meet the quality standards of leather. The leather manufacture process, in turn, generates a variety of solid wastes and stream of wastewater (Bodalo and Gomez, 2007).

The leather processing includes unit operations viz. Pretanning, tanning, post tanning and finishing. It is reported that about 1000 kg of wet salted hides when processed would yield only 200 kg of leather and about 700 kg of solid wastes are generated during the conversion (Chen *et al.*, 2008). The solid wastes generated from the leather industry can be classified into untanned and tanned wastes. The raw trimmings, fleshing wastes (green and limed) and keratin wastes fall into the untanned wastes category (Collivignarelli *et al.*, 1994). Currently the leather industry has to face very high costs to treat and eliminate waste. Worldwide research on leather recycling is directed towards obtaining protein composites by biochemical treatments using microorganism enzymes and obtaining protein hydrolysates and protein binders with different uses. Indeed, leather, even in the form of waste, is a valuable protein source for many areas: automotive industry, agriculture, pharmaceuticals, cosmetics, etc. Organic biopolymers are an important source of raw materials for agriculture, as protein waste composition provides sufficient elements to improve the composition of poor and degraded soils, and plants can benefit from elements such as nitrogen, calcium, magnesium, sodium, potassium (Nogueira *et al.*, 2010).

The European Union (EU) “circular economy” aims to maintain the value of products, materials and resources for as long as possible, minimizing the generation of waste by recycling and reusing them (Eurostat, 2019).

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A way to valorize the untreated hide and skin waste is production of three-dimensional molecular network named, hydrogels, by cross-linking of proteins hydrolyzed with copolymers based on polyacrylamide, polyvinyl alcohol, oligo oxyethylene methacrylate, acrylic acid, maleic acid, cellulose, starch, gum, that form three-dimensional molecular networks. The hydrogels enriched with nutrient C, N, P, K can be used as amendments in agriculture for degraded soils (Puoci *et al.*, 2008; Ramli *et al.*, 2015).

The hydrolyzed collagen represents a high solubility product that could be used in food industry as food supplement or in cosmetic industry for skin care products (Yazaky *et al.*, 2017). By functionalization of collagen hydrolysate with encapsulated nutrients a product with applications as biofertilizers could be obtained (Zainescu *et al.*, 2017).

Collagen hydrolysate added to synthetic polymers could improve the biodegradability of plastic materials (Azeem *et al.*, 2014), and also collagen based-matrices could be successfully cross-linked in order to modify the mechanical properties or the biodegradation rates (Puccini *et al.*, 2010).

This paper presents exploratory research as a starting point to obtain new polymeric complex products - multicomponent - called hydrogels, by processing organic waste with applications in agriculture (Katime *et al.*, 2004).

Obtaining hydrogels with collagen structure by pelt waste hydrolysis with applications in agriculture is a novelty, given that collagen is used only in medicine (Cabeza *et al.*, 1999).

Multicomponent absorbent hydrogel-type networks are next generation materials, with three-dimensional structure and high swelling capacity. The applications of these materials are diversifying, in recent years entering the fields of agriculture, food, pharmaceuticals, electrical devices and electronics, environmental protection and biomaterials (Haiyang *et al.*, 2018). Hydrogels have a distinct three-dimensional structure, and although they have a high water content, hydrogels are water-insoluble due to the crosslinked (physical or chemical) structure of the steric or crystalline linkages. When the hydrogel is in contact with the aqueous solution, there is a swelling thereof.

MATERIALS AND METHODS

In this study, limed hide waste (treated with 1.5% sodium sulfide, 1.3% sodium hydrosulfide and 2.5% calcium hydroxide) was used. Raw hide contains (based on dry weight) 55-70% protein, 0.6 to 9% fat, 20-50% ash and less than 7% water.

The waste came from fleshing and trimming cattle hides (weight category 40 kg) from SC Pielorex tannery in Jilava, Ilfov County, Romania.

The technological process for obtaining smart hydrogel by pelt waste hydrolysis. An innovative process is proposed for treating rawhide waste by protein waste hydrolysis in acid or alkaline medium, to obtain a proteinaceous smart biopolymer which, in combination with other polymers (polyacrylamide, acrylic acid, maleic acid, cellulose, starch, etc.) can be used in agriculture as hydrogels with controlled release of nutrients.

The proposed technological process for obtaining protein hydrogel includes the following:

An amount of 6000 g of pelt waste is washed with water at a temperature of 20-25°C in a drum for 20-30 minutes (as it is strongly alkaline), hide waste is then ground using a special grinder (with double knives), yielding a pasty homogenous mass - protein biopolymer.

The protein biopolymer is introduced together with 3.5-5% dipotassium hydrogen phosphate (which helps to improve the nutritional properties by the addition of phosphorus and potassium) in an autoclave equipped with heating jacket and agitator.

The mixture is stirred for 60-120 min at 75-85°C. Then to this mixture an amount of 1-1.5% boric acid is added and the mixture is removed from the autoclave in plastic drums.

Depending on the fertilizer particle structure, the resulting hydrogel may form the matrix where the fertilizer is embedded or the coating for the solid fertilizer (mono- or multi-layered particles).

RESULTS AND DISCUSSIONS

A hydrogel is defined as a polymer network which has the property of absorbing large amounts of solvent causing macroscopic changes in the dimensions of the polymer. The most important property of hydrogels is their degree of swelling as well as dissolution and gradual release of water and nutrients needed for plant growth.

Characterisation of Compounded Hydrogel

Physical chemical characterization of smart hydrogel is given in Table 1, where for the samples studied the following codes have been allocated:

HC – collagen hydrolysate,

SHC – collagen hydrolysate with nutrients encapsulated.

Table 1. Chemical analysis of tested fertilizers

No	Fertilizer Parameter	UM	HC	SHC	Method of analysis
1	Dry substance	%	24.15	60.18	SR EN ISO 4684: 2006
2	Ash	%	2.35	21.36	SR EN ISO 4047: 2002
3	Total nitrogen	%	10.36	12.55	SR ISO 5397: 1996
4	Soluble phosphorous, P ₂ O ₅	%	-	6.75	SR EN 15959: 2012
5	Soluble potassium, K ₂ O	%	-	10.62	SR ISO 5397: 1996
6	Total organic carbon, TOC	%	46.2	45.2	SR EN 13137/2005
7	pH	units	6.70	7.20	STAS 8619/3-1990

Total phosphorus (P₂O₅), total potassium (K₂O) and total sodium (Na₂O) - were analyzed by extraction through wet mineralization with sulfonated per chloric mixture:

- K₂O and Na₂O were determined by atomic emission spectrophotometry;
- P₂O₅ was determined by molecular absorption spectrophotometry;
- Nt -mineralization and distillation by the Kjeldahl method.

Collagen hydrogels with encapsulated nutrients obtained are delivered in a dry state, packed in polyethylene bags accompanied by instructions for use.

This experimental model can establish a technology for converting pelt waste into collagen hydrogels with encapsulated nutrients, which can be used as fertilizers in agriculture (especially in horticulture).

The hydrogels were analyzed in terms of structure and elemental composition using modern instrumental methods, namely SEM-EDAX electron microscopy. Examination of collagen hydrogel samples with encapsulated nutrients by SEM EDAX shows the

appearance of crosslinking centres and the formation of collagen-starch or collagen-polyacrylamide compounds can be seen.

Figure 1. Elemental analysis by electron microscopy of smart hydrogel

SEM-EDAX micrographs of collagenic hydrogels with encapsulated nutrients for soil fertilization, showing the fibrillar collagenic structure with nutrient crystals - phosphorus, potassium, magnesium, etc., are shown in Figure 1.

In conclusion, this work can establish a technology for converting pelt waste into collagen hydrogels with encapsulated nutrients, which can be used as fertilizers in agriculture, to remedy degraded soils.

Soil conditioning consists in improving the physical properties by using substances of various origins, known in the specialized literature as soil conditioners.

To highlight the structural changes in the process of hydrolysis and interaction with various synthetic polymers, attenuated total reflectance spectrophotometer FT/IR-ATR, Perkin Elmer, USA, was used.

Molecular absorption spectrometry in the infrared IR is based on vibration-rotation transitions that occur at the molecular level by absorbing infrared radiation. From IR spectra chemical bonds and the molecular structure of organic compounds may be identified. The bands specific for collagen are similar to those of other proteins. The IR spectrum shows bands of the amide I, II and III at about 1660, 1550 and 1240 cm^{-1} , respectively.

Figure 2. IR spectrum of the hydrogel, collagen/smart hydrogel

Hydroxyl groups and the hydrogen bonds are recorded between 3600 and 3100 cm^{-1} . According to the spectral assignments, in the case of collagen hydrolysate, bands were observed corresponding to amide groups ($\nu_{\text{C=O}}$ 1645 cm^{-1} to δ_{NH} and $\nu_{\text{C-N}}$ 1556 cm^{-1}).

Also, the characteristic signals of NH groups are present at 1338 cm^{-1} . OH groups in units of hydroxyproline, are signalled at 1082 cm^{-1} . Therefore, the bands at 1660 to 1550 cm^{-1} , by their position and absorbance, give information on the degree of degradation. Hydrolysis of the chain is marked by changes in the band from 3450-3200 cm^{-1} region that tends to broaden and change its transmittance; at the same time, the band at 1660 cm^{-1} increases in intensity, because its structure includes a -OH component, and the band at 1550 cm^{-1} decreases in intensity. In the collagen hydrolysates, some of the OH groups are replaced with methoxide groups, (CH_3), which attenuate the hydrogen bonds and decrease the crystallinity of the collagen while increasing the water solubility.

CONCLUSIONS

A comprehensive study is presented on recycling hide waste resulted from leather industry by capitalising their valuable protein components to obtain efficient collagen-based hydrolysates as smart fertilizers for poor soils amelioration. Hydrogels as controlled fertilizer release systems in agriculture have major advantages in that they combine water absorption and its slow release with nutrients (N, M, P, Fe, Zn, B, etc.) necessary for plant growth. The fertilizer quality is mainly conferred by the content in NPK nutrients available for plant growth and their leaching in soil solutions.

A framework technology was established for obtaining hydrogels with collagen structure from pelt waste.

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REFERENCES

- Azeem, B. *et al.* (2014), "Review on materials and methods to produce controlled release coated urea fertilizer" *Journal of Controlled Release*, 11–21, <https://doi.org/10.1016/j.jconrel.2014.02.020>.
- Bódalo, A. and Gómez, J.L. (2007), "Study of the evaporation process of saline waste from the tanning industry", *Waste Manag.*, 25, 467-474, <https://doi.org/10.1177/0734242X07079869>.
- Cabeza, L.F. *et al.* (1999), "Isolation of protein products from chromium-containing leather waste using two consecutive enzymes and purification of final chromium product: pilot plant studies", *J. Soc. Leather Technol. Chem.*, 83, 14-19.
- Chen, C. *et al.* (2008), "Development of comprehensive utilization of leather solid waste", *Leather Sci. Eng.*, 18, 27-33.
- Collivignarelli, C. *et al.* (1984), "Waste recovery in the tanning industry". *Waste Manag. Res.*, 2, 265-278, <https://doi.org/10.1177/0734242X8400200130>.
- Eurostat (2019), "Circular economy in the EU, Record recycling rates and use of recycled materials in the EU", 39/2019, available at: <https://ec.europa.eu/eurostat/documents/2995521/9629294/8-04032019-BP-EN.pdf/295c2302-4ed1-45b9-af86-96d1bbb7acb1>.
- Haiyang, Y. *et al.* (2018), "Synthesis and self-assembly of multiple-responsive magnetic nanogels", *Polymers for Advanced Technologies*, 30(2), 312-319, <https://doi.org/10.1002/pat.4467>.
- Katime, I. *et al.* (2004), *Los materiales inteligentes de este milenio: Los hidrogeles macromoleculares. Síntesis, propiedades y aplicaciones*, Servicio Editorial de la Universidad del País Vasco, España.

<https://doi.org/10.24264/icams-2020.IV.4>

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- Nogueira, F.G.E. *et al.* (2010), "Incorporation of mineral phosphorus and potassium on leather waste (collagen): A new N_{collagen}PK-fertilizer with slow liberation", *Journal of Hazardous Materials*, 176 374–380, <https://doi.org/10.1016/j.jhazmat.2009.11.040>.
- Puccini, M. *et al.* (2015), "Utilization of starch films plasticized with urea as fertilizer for improvement of plant growth", *Chemical Engineering Transactions*, 43, 7005-7010.
- Puoci, F. *et al.* (2008), "Polymer in Agriculture: a Review", *American Journal of Agricultural and Biological Sciences*, 3(1), 299-314, <https://doi.org/10.3844/ajabssp.2008.299.314>.
- Ramli, N.K. *et al.* (2015), "A comprehensive review on biodegradable polymers and their blends used in controlled release fertilizer processes", *Rev Chem Eng*, 31(1), 69–95, <https://doi.org/10.1515/revce-2014-0021>.
- Yazaki, M. *et al.* (2017), "Oral Ingestion of Collagen Hydrolysate Leads to the Transportation of Highly Concentrated Gly-Pro-Hyp and Its Hydrolyzed Form of Pro-Hyp into the Bloodstream and Skin", *J. Agric. Food Chem.*, 65, 2315–2322, <https://doi.org/10.1021/acs.jafc.6b05679>.
- Zainescu, G. and Constantinescu, R.R. (2017), "Smart hydrogels with collagen structure made of pelt waste", *Rev. Chim. (Bucharest)*, 68(2), 393-395, <https://doi.org/10.37358/RC.17.2.5461>.