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SMART BIOCONVERSION OF PELT WASTE FROM TANNERIES

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Abstract: *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. Leather processing in tanneries results in about 500-600 kg of pelt waste from a ton of raw hides.*
These hydrogels are made using smart processes in order to then be applied in agriculture, for preservation of water in the soil or for controlled release of fertilizers, pesticides but also for the development of additivated agricultural film biodegradable over time (between 1 month and 6 months). Hydrogels that are based on biopolymers, compared with hydrogels based on synthetic polymers, have the advantage of biodegradability, biocompatibility, and a low level of toxicity.
The paper presents the production of biodegradable polymer mixtures obtained from hydrolysis and enrichment of the resulting hydrolysate with phosphorus and potassium.
Hydrogels with collagenous structure are tested using a high-performance instrumental analysis system (FT-IR-ATR, UV-VIS-NIR, SEM, EDAX, etc).
The paper presents an experimental model for obtaining hydrogels with collagenous structure from pelt waste resulting from the liming process.

Key words: biopolymers, hydrogels, collagen, tannery, soil.

1. INTRODUCTION

Biopolymers of organic nature are a source of raw materials for agriculture, as protein waste composition provides sufficient elements to improve the composition of degraded soils and plants can harness some elements: nitrogen, calcium, magnesium, sodium, potassium, etc.

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.

The paper contributes both to the reuse of poor and degraded soils in agriculture and to the recovery of protein waste which is currently disposed of in landfills (processing 1 ton of raw hide results in 75% waste, of which about 50% - approximately 600 Kg - is protein waste that can be used in agriculture) [1-3].

Obtaining hydrogels with collagen structure by pelt waste hydrolysis with applications in agriculture is a novelty, given that collagen is used only in medicine.

Multicomponent absorbent hydrogel-type networks are next generation materials, with three-dimensional structure and high swelling capacity. Hydrogels have a distinct three-dimensional structure [4-7], 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.

Hydrogels can be obtained by two major mechanisms: hydrogels with covalent or irreversible links and hydrogels with reversible or physical links [8,9]. The second category includes various subclasses such as ionic interactions (ionic hydrogels or cross-linked polyelectrolyte complexes) and secondary interactions ("entangled" hydrogels, grafted or complexed hydrogels, etc.) [10-11].

In the past decade, interest in different types of gels in areas such as pharmaceuticals, food chemistry, medicine and biotechnology has increased.

2 EXPERIMENTAL

The applications of hydrogels in agriculture aim at water retention in the soil or controlled release of pesticides or fertilizers. In the first case, the application is based on hydrogels' ability to quickly absorb large amounts of water and then release it gradually, supplying plants with water for longer periods after watering the field (rain or irrigation) has ceased.

Currently, most hydrogels are based on synthetic polymers, so this research proposes the use of collagen hydrolysate obtained from pelt waste (HA) and a synthetic copolymer based on polyacrylamide (CAAM).It is known that polyacrylamide is a crosslinked polymer that retains its hydrophilic nature and can absorb a large amount of water and increase its volume. Some of the advantages of hydrogels based on acrylamide include being chemically inert, transparent and stable in a wide range of pH, temperature and ionic strength. CAAM copolymer based on polyacrylamide is a granular anionic polyelectrolyte with high molecular mass produced in Germany.

In this research, synthesis of hydrogels is reported to CAAM and HA by chemical crosslinking using different concentrations and crosslinking agents, polymers of different ratios to determine the effect of variations in the hydrogel and establish the optimal reaction conditions. Then characterization techniques were performed to determine the thermal, structural, morphological and swelling capacity of the hydrogels.

The waste came from fleshing and trimming cattle hides (weight category 35 kg) from SC Pielorex tannery in Jilava, Ilfov County, Romania.

An innovative process is proposed for treating rawhide waste by protein waste hydrolysis in acid or alkaline medium, to obtain a proteinaceous 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:

1. A quantity of 4.5 to 6.0 kg of pelt waste is washed with water at a temperature of 20-25 ^{0} C in a drum for 20-30 minutes (as it is strongly alkaline)

2. Hide waste is then ground using a special grinder (with double knives), yielding a pasty homogenous mass - protein biopolymer.

3. The protein biopolymer is introduced together with 5 to 6.5 % 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 85-96 ^{0} C

4. Then to this mixture an amount of 18 to 25 % of a synthetic polymer based on polyacrylamide is introduced and stirring is continued for 120-180 minutes.

5. 0.5-1% 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).

2. 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.

Hydrogels reduce water consumption and irrigation allotted time by 70 %. The hydrogel is an organic soil conditioning substance, which retains the water and diluted nutrients necessary to these plants. Hydrogel in an optimum amount helps plant growth by releasing the necessary water and nutrients.

Hydrogel binds the water and nutrients in the water and continuously provides them to the roots of the plants.

Table 1. *Physical-chemical analyses of hydrogel*

No.	Specification of components	UM	Values reported to relative humidity upon release
1	Total nitrogen (Nt)	%	12,74
2	Phosphorus (P_2O_5)	%	3,64
3	Potassium (K_2O)	%	6,18
4	Sodium (Na_2O)	%	0,37
5	pH	pH units	6,8

- K_2O and Na_2O were determined by atomic emission spectrophotometry
- P2O5 was determined by molecular absorption spectrophotometry
- Nt -mineralization and distillation by the Kjeldahl method

Chemical analysis of collagen structure hydrogel for field experiments resulted in $N_{12}P_9K_{12}$ composition (12.74% total nitrogen, phosphorus, 3.64% P_2O_5, potassium K_2O_5 6.18%)(**Table1**).

Hydrogels were studied in terms of structure and composition using modern instrumental methods. Hydrogels obtained both at laboratory and pilot scale were analyzed using modern equipment at INCDTP and ICMPP-Petru Poni Iasi.

SEM-EDAX micrographs of collagen hydrogels with encapsulated nutrients for soil fertilization, wherein the fibrillar collagen structure is observed, showing crystals of nutrients - phosphorus, potassium, magnesium, etc. are shown in Figures 1 and 2.

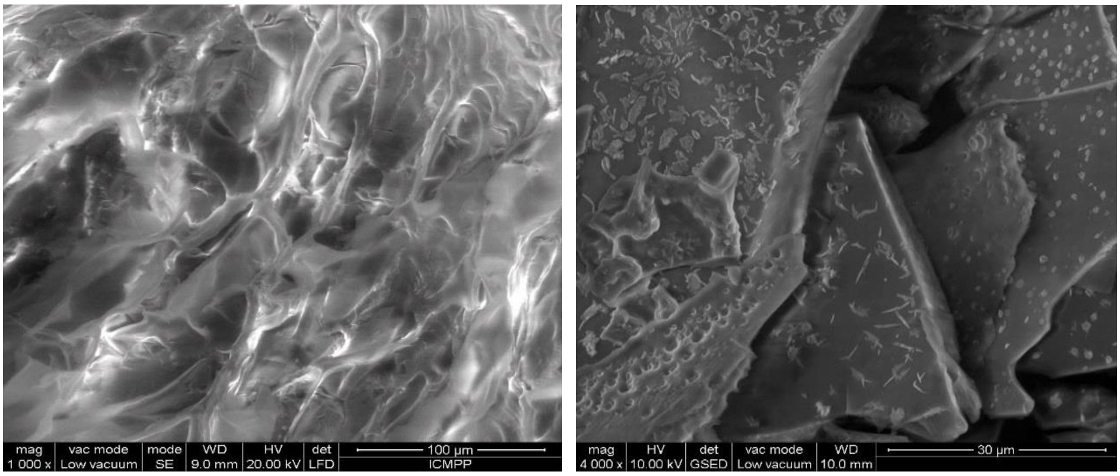

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Fig.1. *SEM micrographs of hydrogel with encapsulated nutrients*

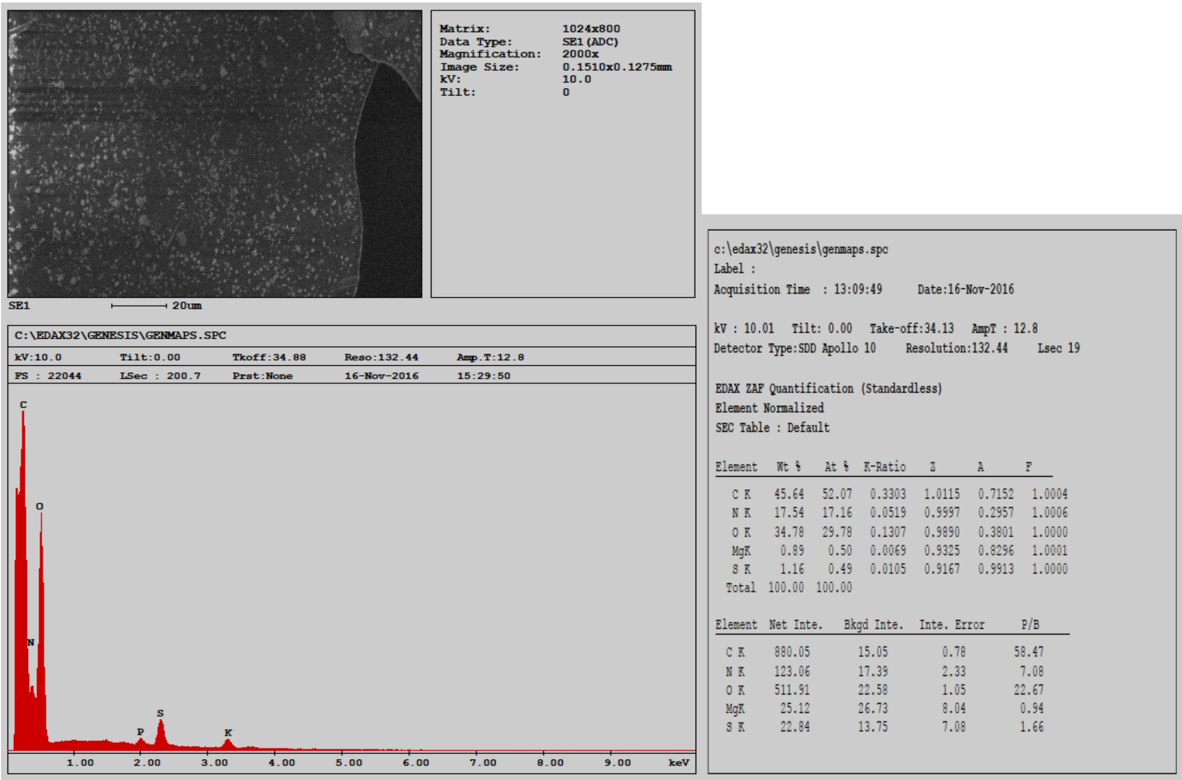

Fig.2. *EDAX analysis of the structural composition of the hydrogel*

In order to highlight the structural changes in the hydrolysis process and the interaction with various synthetic polymers, attenuated total reflectance spectrophotometer FT/IR-ATR Perkin Elmer, USA was used. As Figure 6 shows, all bands specific to the polypeptide matrix of collagen can be identified, such as those at 1658 cm^{-1} and 1541 cm^{-1} (amide I and amide II bands, respectively), while those at 3406 cm^{-1} and 1030 cm^{-1} indicate the C-N bond.

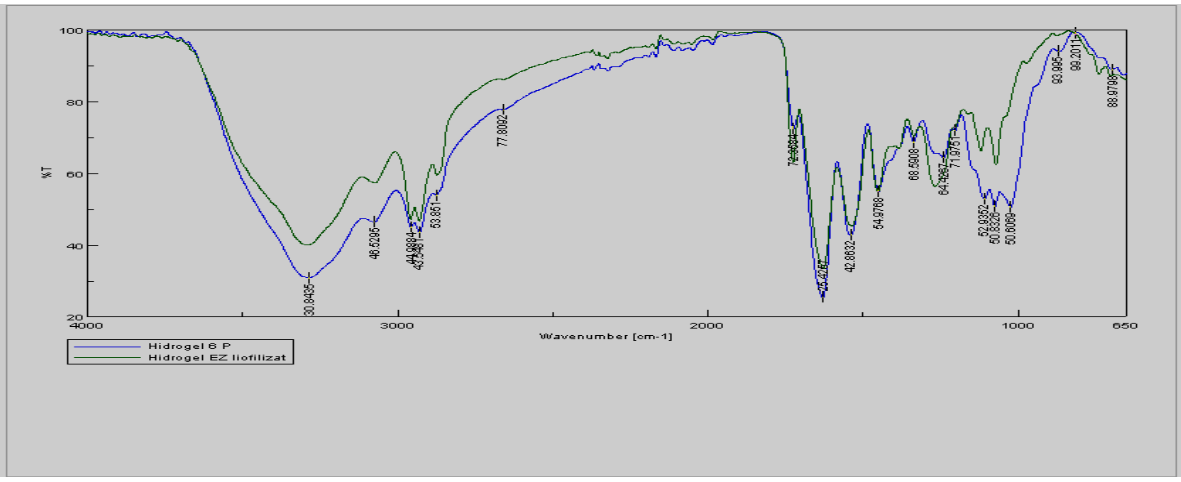

Fig.3: *IR spectra for hydrogels*

The difficulty in interpretation of spectral diagrams arises due to the structural complexity of collagen compositions and the use of trace elements, which have chemical affinity for the same functional groups of the respective macrostructure.Thus, the presence of collagen and acrylamide is confirmed in the molecular structure of the hydrogel.

4. CONCLUSIONS

The paper presented in detail two framework technological pilot-scale processes, of the direct hydrolysis of pelt waste

Hydrogels obtained both at laboratory and pilot scale were studied in terms of structure and composition using modern instrumental methods **(**optical microscopy, scanning electron microscopy SEM-EDAX, FT/IR-ATR, Differential Scanning Calorimetry (DSC)).

In conclusion, the obtained hydrogels show encapsulation of nutrients and the emergence of cross-linking junctions with macro- and microelements introduced in the direct hydrolysis reaction. This confirms the presence of collagen and acrylamide into the molecular structure of the hydrogel by forming collagen-polyacrylamide compounds.

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