

Study on the Levigation Ability of Nutrients for Soils Treated with Titanium-containing Biopolymers

GABRIEL A. ZAINESCU¹, RODICA ROXANA CONSTANTINESCU^{1*}, PETRE VOICU², DANA C. DESELNICU³

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

² Research Institute for Soil Science and Agrochemistry, 61 Marasti Blvd., 011464, Bucharest, Romania

³ University Politehnica of Bucharest, Faculty of Entrepreneurship, Business Engineering and Management (FAIMA), 313 Splaiul Independentei, 060042, 1-7 Gh. Polizu, 011061, Bucharest, Romania

The paper refers to obtaining protean biopolymers from Ti – tanned leather waste and it also to studying the levigation ability of nutrients for soils treated with titanium-containing biopolymers. Using tanned waste is of particular interest because it offers the opportunity to eliminate all wastes from tanning, while obtaining qualitatively and economically valuable products. Organic biopolymers represent a source of raw material for agriculture, because the composition of protean wastes provides enough elements to improve composition and rehabilitation of degraded soils, and plants can capitalize some elements: nitrogen, calcium, magnesium, sodium, potassium, titanium etc. The wastes used for this innovative procedure for obtaining biopolymers, are obtained from wet white tanned leather through a new technique based on Ti-Al tanning agents. The aim of protein waste hydrolysis is to obtain new products, state-of-the-art protein fertilizers and soil improvers designed to potentiate the transfer of nutrients obtained from the protein soil improver to plant and fruit, with the effect of stimulating the metabolism, speeding up the productive phase, stimulating the defense system of the plant and optimizing mechanisms responsible for the health of the fruit.

Keywords: biopolymers, organic wastes, tannery, soil

This paper deals with agrochemical basics of applying biofertilizers and degraded soil improvers, analyzing the mechanism and dynamics of penetration of nutrients in plants, their influence on plant growth and development to give high yields and high quality crops, and agrochemistry of nutrients. The agrochemistry of each element is dealt with through the soil-plant-protein biofertilizer interaction.

Environmental restrictions in agriculture require organic farming by discarding classic fertilizers. To this end, research on unconventional fertilizers intensified, from the liquid to the extraradicular (foliar) ones, at the same time establishing application technologies. Thus, these fertilizers have currently a share of approx. 30-35% in the balance of substances used for fertilization and their use is a current policy of the European Community in order to promote sustainable organic farming and to reduce environmental and groundwater pollution [1,2].

The most remarkable advantage of using protein fertilizers and soil improvers obtained from pelt waste is the positive impact, demonstrated by the development and health of plant, as well as by its resistance to stress factors (drought, salts and pesticides) [3-5].

These benefits are the result of high cation exchange capacity, pH buffering capacity and increased water retention capacity. Through their collagen content, protein fertilizers and soil improvers stimulate the activity of beneficial organisms in the soil (earthworms in particular). Because of these excellent properties they may be used in all types of soil and all plant species, stimulating growth and development, and thus the harvest yield [6-9].

Protein fertilizers and soil improvers obtained from pelt wastes have the following advantages:

increase production and improve plant quality, stimulate enzymatic substances in the plant, improve and stimulate the volume and activity of beneficial microorganisms in

the soil, increase cation exchange capacity (CEC), foster development of root system, increase permeability of cell membranes in the root system, fostering absorption/retention of nutrients, act, in the case of alkaline soils, as a natural chelating agent for micronutrients, fostering their accessibility to plants, reduce stress caused by drought, salinity or by application of treatments with phytosanitary products, increase germination capacity of seeds and foster development of rootlets, reduce the amount of toxic or herbicide residues in the soil, delay decomposition of unstable substances under UV ray action [10-15].

Application of protein soil improver from pelt waste can correct boron deficiency, prevents and corrects weak fruiting and leaf malformations. It also significantly increases phosphorus uptake, improves vegetative development and cell wall formation, increasing pollen fertility and resistance of plants to low temperatures.

In the pelt waste hydrolysis process, magnesium can be added (up to 1.5%), thus the protein fertilizer will be recommended for use in early development of plants to induce normal flowering.

Experimental part

Biotechnology of obtaining protein biocomposites consists mainly of hydrolysis of untanned hide waste (pelt) using basification and enrichment agents and/or enzymatic commercial products in order to apply them as soil improvers and fertilizers.

An innovative process for acid hydrolysis of titanium-containing wet white leather waste was developed in ICPI pilot plant, resulting in a proteic biopolymer in two variants, a dried one, named Biopolymer 1, and a freeze-dried one, named Biopolymer 2 (different K and P content).

The technological framework process to obtain proteic biopolymers from titanium-containing wet-white leather

* Tel.: 0742423688

No.	Determination	M.U.	Values obtained	Testing method
1	Total nitrogen (Nt)	%	6.97	CE 2003/2003 regulation annex IVB - Met. 2: 2.6; 2.6.2(PTL 02 – Method B)
2	Total phosphorus (P ₂ O ₅)	%	1.65	Determination through atomic absorption spectrometry from the extract obtained by wet mineralization with sulfo-perchloric mixture
3	Water soluble potassium (K ₂ O)	%	21.97	Flame photometric determination from the extract obtained by wet mineralization with sulfo-perchloric mixture
4	pH of solution, concentration 0,25 %	pH units	7.62	Potentiometric method
	pH of solution, concentration 0,50 %		7.60	
	pH of solution, concentration 1 %		7.55	
	pH of solution, concentration 5 %		7.43	
	pH of solution, concentration 10 %		7.37	
5	Conductivity of solution, concentration 0,25 %	mS/cm	1.81	Conductometric method
	Conductivity of solution, concentration 0,50 %		3.49	
	Conductivity of solution, concentration 1 %		6.51	
	Conductivity of solution, concentration 5 %		27.0	
	Conductivity of solution, concentration 10 %		47.20	
6	Electric conductivity (extraction ratio 1:10)		46.85	
7	Total soluble salts (extraction ratio 1:10)	g/100 material	32.80	Calculated from electric conductivity

Table 1
PHYSICO-CHEMICAL
CHARACTERISTICS -
BIOPOLYMER 1 SAMPLE

No.	Determination	M.U.	Values obtained	Testing method
1	Total nitrogen (Nt)	%	10.13	CE 2003/2003 regulation annex IVB - Met. 2: 2.6; 2.6.2(PTL 02 – Method B)
2	Total phosphorus (P ₂ O ₅)	%	3.43	Determination through atomic absorption spectrometry from the extract obtained by wet mineralization with sulfo-perchloric mixture
3	Water soluble potassium (K ₂ O)	%	2.35	Flame photometric determination from the extract obtained by wet mineralization with sulfo-perchloric mixture
4	pH of solution, concentration 0,25 %	pH units	3.81	Potentiometric method
	pH of solution, concentration 0,50 %		3.70	
	pH of solution, concentration 1 %		3.63	
	pH of solution, concentration 5 %		3.50	
	pH of solution, concentration 10 %		3.43	
5	Conductivity of solution, concentration 0,25 %	mS/cm	1.32	Conductometric method
	Conductivity of solution, concentration 0,50 %		2.49	
	Conductivity of solution, concentration 1 %		4.63	
	Conductivity of solution, concentration 5 %		18.97	
	Conductivity of solution, concentration 10 %		32.90	
6	Electric conductivity (extraction ratio 1:10)		31.30	
7	Total soluble salts (extraction ratio 1:10)	g/100 material	21.91	Calculated from electric conductivity

Table 2
PHYSICO-CHEMICAL
CHARACTERISTICS -
BIOPOLYMER 2 SAMPLE

waste (shavings), was the following: 6000 g titanium-containing wet-white leather waste (shavings) were weighed, then mixed with 12-15 l water and subjected to

a pretreatment by adding 2-5 % NaCl for 1-3 h. The mixture is hydrolysed in a 50 l autoclave with double jacket and

stirrer, adding 3-7 % K_2HPO_4 and 5-10 % concentrated HCl (37%) at a temperature of 90-98°C for 2.5 - 5 h.

The titanium-containing hydrolysate is then mixed with 20-45% collagen hydrolysate obtained from pelt waste. The proteic biopolymers thus obtained are delivered either in liquid form, in plastic barrels, or dried and packed in polyethylene bags accompanied by instructions for use.

Results and discussions

Physical-chemical analyses consisted in determining nitrogen, phosphorus, potassium, pH, electric conductivity and total soluble salt content for Biopolymer 1 and 2, as well as meso and micronutrient (Cu, Zn, Fe, Mn and Mg) determinations, presented in tables 1 and 2.

Physical-chemical analyses were performed in the Fertilizer Quality Control and Testing Laboratory, accredited by RENAR (LI no. 673/2013). The methods used in the laboratory (according to CE 2003/2003 regulations) were adapted, given the organic matrix of the biopolymer, as well as data from Methodology of Agrochemical Analysis of Soils in Order to Establish the Necessary Amendments and Fertilizers, vol. I, Bucharest, 1981.

Biopolymers 1 and 2 were also subjected to levigation tests.

Standardised tests to characterise slow-release fertilizers and techniques to determine the degree of levigation into the soil, identified and implemented to be used are defined mainly by reference of:

- SR EN 13266 / 2002 "Slow-release fertilizers - Determination of the release of the nutrients";
- SR CEN/TR 14405 / 2009 "Characterization of waste - Levigation behaviour tests - Up-flow percolation test (under specified conditions)".

European Standard SR EN 13266 / 2002 specifies a method to determine slow solubilization (release) properties of nutrients in encapsulated fertilizers. Hydrolysis processes depending on pH and biological and microbial degradation are excluded.

Standard SR CEN/TR 14405 / 2009 - "Characterization of waste - Levigation behaviour tests - Up-flow percolation test (under specified conditions)", also applicable to fertilizers, describes a method to determine release of constituents from waste, solid materials, with or without reducing particle size, loaded in a percolation column. The sample to be tested is loaded in a column in a standardized manner. The levigation solution is percolated in an upward or downward flow through the column at a flow rate defined by a preset L/S ratio. The eluate is collected in separate fractions which are physically and chemically characterized in accordance with existing standardized testing methods. In experiments, equilibrium conditions from discharging and washing the column are checked after a period of equilibration by measuring pH value.

Test results are expressed in functions of L/S ratio, in terms of mg of released constituents per litre of eluate, and mg of constituents released cumulatively per kg of dried material.

Scheme 1 presents loading of the levigation/percolation column with the biopolymer in the soil.

To load levigation columns (with 60 mm diameter), the following operations are performed:

- 250 g of sandy soil (Dăbuleni) are added over the frit plate of the column;
- the multifunctional sensor is installed - in the middle, vertical to the column generator;
- the second portion of sandy soil (320 g) is then added;
- the biopolymer-based fertilizer (0.5 g) is uniformly distributed over the soil layer;
- the last portion of sandy soil (250 g) is added;

Column top
Sandy soil ↓ 250 g
Tested biopolymer 0.5 g
Sandy soil ↓ 320 g
Multifunctional sensor
Sandy soil ↓ 250 g
Column base

Scheme 1
Loading the 60 mm diameter column with Biopolymer

- the column thus loaded is gently tapped to arrange and settle soil layers;

- a filter paper designed to uniformly disperse the water is placed on top of the soil layer;

- the levigation column is attached to a vertical base, a funnel and a glass are placed under the column to collect daily fractions.

After loading, columns are wetted with 150 mL distilled water and left to rest until the next day, when the proper levigation is started.

A scheme of the experiment is presented in table 3.

Table 3

VARIANT	Repetitions
Control, soil without biofertilizer	3
Biopolymer 1	3
Biopolymer 2	3

Each of the 9 levigation columns were wetted daily with 40 mL distilled water, and volume, pH and conductivity were determined for the solutions collected. After 5 days of levigation, solutions collected for each variant are gathered into a single extract. Volume, pH and conductivity are determined for this extract as well, in addition to administering nitrogen, phosphorus and potassium.

Throughout the experiment period of 39 days, 25 eluent solutions were collected and analysed in terms of pH and conductivity. These determinations were performed for control, Biopolymer 1 and Biopolymer 2 samples. The evolution of physical parameters measured (conductivity) over time for control, Biopolymer 1 and Biopolymer 2 samples is presented below.

Figure 1 show that pH values have decreased for all 3 variants, varying between 7.79 and 6.98 for the control sample, between 6.39 and 7.84 for Biopolymer 1 and between 6.11 and 8.01 for Biopolymer 2.

Figure 2 show that the evolution of electric conductivity for eluent solutions of the three variants (control, Biopolymer 1 and Biopolymer 2) is approximately the same.

This is demonstrated by the significantly distinct correlation degree between their values, namely:

i. $r = 0,934$ for values of Control and Biopolymer 1 variants;

ii. $r = 0,943$ for values of Control and Biopolymer 2 variants;

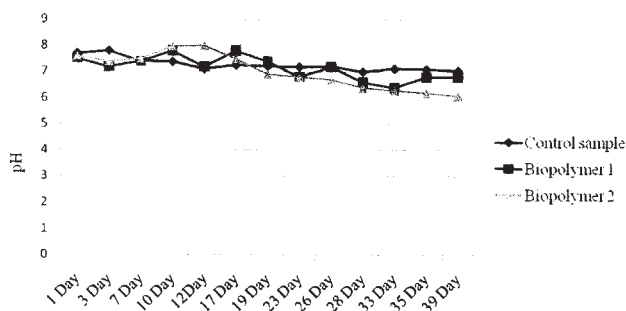


Fig. 1. Evolution of pH values in levigation solutions over time for control sample, Biopolymer1, Biopolymer 2

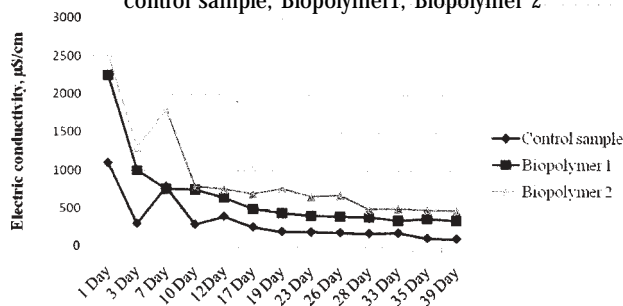


Fig. 2. Evolution of electric conductivity values for levigation solutions over time for control sample, Biopolymer1, Biopolymer2

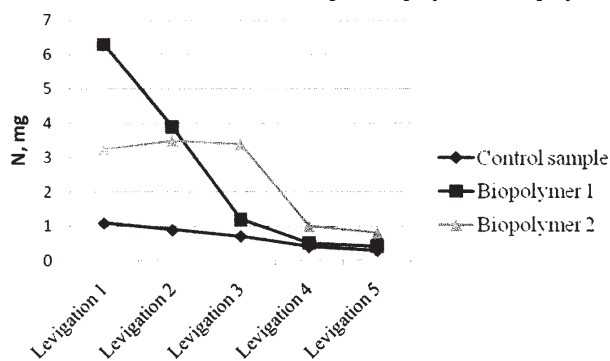


Fig. 3. Evolution of nitrogen concentration values (N, mg) in levigation solutions over time for control sample, Biopolymer 1, Biopolymer 2

iii. $r = 0,985$ for values of Biopolymer 1 and Biopolymer 2 variants;

The 5 consecutive levigation solutions collected for each variant for 39 days from 25 collections, were mixed for chemical and physical analyses. Of the resulting 5 levigation solutions collected, nitrogen (N), phosphorus (P_2O_5) and potassium (K_2O) content was measured. Their concentration was expressed in mg collected of each element.

The evolution of nitrogen, phosphorus and potassium (mg) concentrations over time from the 5 eluent solutions is presented below (fig 3-5).

Figures 3, 4 and 5 show that values of nitrogen, phosphorus and potassium concentrations decrease over time (correlation between values is 0,988). In the case of phosphorus a slower release is noticed, knowing that its mobility in the soil is much lower than that of nitrogen and potassium (due to its tendency to form low solubility compounds).

In the case of Biopolymer 1, evolution of nitrogen concentration values (N) decreases from 6.3 to 0.33 mg (fig. 3).

In the figure 4, the lowest variation of concentrations collected in the 5 levigation solutions was recorded for phosphorus (from 2.7 to 2.1).

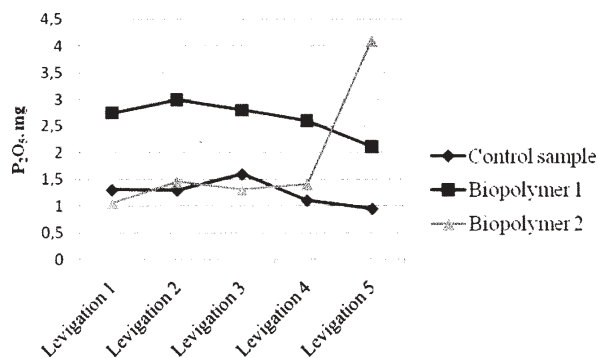


Fig. 4. Evolution of phosphorus concentration (P_2O_5 , mg) in levigation solutions over time for control sample, Biopolymer 1, Biopolymer 2

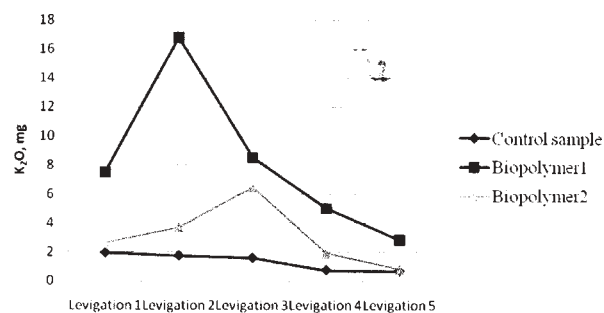


Fig. 5. Evolution of potassium concentration (K_2O , mg) in levigation solutions over time for control sample, Biopolymer 1, Biopolymer 2

Conclusions

The product according to the paper is obtained through biotechnologies applied to wet white leather waste and are effective in improving quality of degraded soils and stimulating plants and fruits metabolism. Organic biocomposites are a source of raw materials for agriculture, because their composition provides sufficient elements to improve chemical and physical characteristics of degraded soils, as well as plant growth.

The novelty of this paper is based primarily on soil science applications of protein biocomposites obtained from titanium-containing wet white leather waste by compounding with biodegradable polymers. New product composition: Organic substances: 38-83%; NPK 12-9-12; $pH = 3.8-7.9$. The water-soluble product is applied in the soil or by means of the irrigation system by dripping or by foliar application. When applying by dripping, over-irrigation 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 and on degraded soils

In conclusion, as a result of testing experiments on degraded soils treated with proteic biopolymers from titanium-containing wet white leather waste (Biopolymer 1 and Biopolymer 2) regarding levigation of nutrients, biopolymers were found to have a very good behaviour as soil improvers.

Acknowledgements: This work was supported by the European Fund for Regional Development and the Romanian Government in the framework of Sectoral Operational Programme under the project INNOVA-LEATHER: "Innovative technologies for leather sector increasing technological competitiveness by RDI, quality of life and environmental protection" - contract POS CCE-AXIS 2-O 2.1.2 nr. 242/20.09.2010 ID 638 COD SMIS- CSNR 12579.

References

1. ZAINESCU, G., BARNA, V., CONSTANTINESCU, R., BARNA, E., VOICU, P., SANDRU, L. *Mat. Plast.*, **48**, no. 4, 2011, p. 295
2. ZAINESCU, G., DESELCU, D. C., IOANNIDIS, I., CRUDU, M., VOICU, P., 4th International Conference on Advanced Materials and Systems, Romania 2012, pp 71.
3. CONSTANTINESCU, R. R., NICHITA, P., MEGHEA, A., ZAINESCU, G., SIRBU, C., *Rev. Celuloza si Hartie*, 62, nr.3, 2013, p.28
4. GURLER, D., KILIC, E., 4th International Conference on Advanced Materials and Systems, Romania 2012, p. 273.
5. USHARANI, N., JAYAKUMAR, C. G., KANTH, V. S., RAO, J. R., *Biopolymers* 101, nr.8, 2014 p. 903.
6. EGEMOSE, S., JENSEN, H.S., *Reser. Manage.* 25, 2009 p.4.
7. *** PATENT RO 127100 B1 , 2014.
8. ZAINESCU, G.A., VOICU, P., CONSTANTINESCU, R., ARSENE, M., VIZITIU, O., MIHALACHE, M., XIII International Waste Management and Landfill Symposium- Sardinia 2011
9. PÉREZ-LIMIÑANA, M.A., ESCOTO-PALACIOS, M.J., MARTÍNEZ-SÁNCHEZ, M.A., FERRER-PALACIOS, J., ARÁN-AÍS, F., ORGILÉS-BARCELÓ, C., The 5th International Conference on Advanced Materials and Systems , 2014 p. 479
10. ZAINESCU, G.A., MIRCEA, M., VOICU, P., CONSTANTINESCU, R.R., ILIE, L., OBRISCA, M., *Scientific Papers, UASVM Bucharest, Series A*, 2011, p.89
11. BACARDIT, A., BAQUERO, G., SOROLLA, S., OLLÉ, L., *Journal Cleaner Production*, 101, 2015, p197
12. DIXIT, S., YADAV, A., DWIVEDI, P. D., DAS, M., *Journal of Cleaner Production*, 87, 2015, Pages 39-49
13. SIRBU, C., CIOROIANU, T., DUMITRU, M., DORNEANU, A., NEGRILA, M., MIHALACHE, D., ANGHELESCU, L., *Lucrări ştiinţifice*, 51, *Agronomie* 2009, p 189
14. KATKAT, A. V., ÇELIK, H., TURAN, A. M., ASIK, B. B., *Australian Journal of Basic And Applied Sciences*, 3(2): 1266-1273, 2009
15. MADARAS, M., KOUBOVÁ, M., SMATANOVÁ, M., *Plant Soil Environ*, 60, 2014, No. 8: 358-363

Manuscript received: 30.06.2015