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BIOPOLYMERS SYSTEMS FROM LEATHER WASTES FOR DEGRADED SOILS REMEDIATION

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Abstract

Most tanneries and leather product manufacturers have serious problems regarding waste discharge, as their disposal in dump wastes leads to chromium accumulation in soil with possible harmful effects on the ecosystem.

The use of untanned wastes presents a special interest, because it provides almost total fleshing waste discharge while obtaining qualitatively and economically valuable products.

The main target of this scientific paper is investigating the development possibilities for various multicompound systems of biodegradable polymers and studying the effects of these complex products on the structure and chemical and physical characteristics of degraded or contaminated soils (having a poor level of organic matter or submitted to a strong erosion process).

The paper presents a new pilot technology for biochemical decay of the tannery protein wastes and use of the resulted products as fertilizers. In the present paper, the agrochemical base of biofertiliser use is investigated, analyzing the principle and dynamics of nutrient elements penetrating soil and plants, their influence on weathered soil rehabilitation/conditioning and on plant growth and development, as well as in agrochemistry of nutritive elements.

INTRODUCTION

The exploitation of protein wastes from tanneries is a necessity of ecologic technologies, as the largest waste amount resulting from leather processing is that of untanned wastes. It is known from technological practice that, as a result of processing a ton of raw hide, wastes are 75% of which 50% are protein wastes which can be used in agriculture, as biofertilizer [1].

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

Biodegradable polymers - organic polymers - are among soil conditioners with multiple advantages.

Soil contamination means a moderate increase of elements/substances which are not harmful for plant growth and development, but which can represent the initial phase of the pollution process. Reducing the effects of degradation/contamination/ pollution consists in applying remediation methods, of improving the characteristics of soil affected by degradation processes or by limitative factors, for the purpose of recovering to the original state of fertility and productivity, to a higher or at least similar state to the initial one.

Remediation refers to methods to be applied on terrains that are not suitable for agricultural or forest use, such as some dumps from mining or various residues, in order to recycle them into the environmental circuit.

In general, polyelectrolytes (such as polyelectrolytes based on polyacrylamide), as well as other categories of synthetic polymers, contribute to the improvement of soil characteristics through one or more of the following effects:

- increasing the degree of aggregation of structural elements of soils with degraded structure
- preventing crust formation in the period between plant seeding and emergence, particularly in those with small seeds, which are very vulnerable;
- increasing resistance to water and air erosion of soils situated on slopes and those with coarse structure (clay under 12%);
- preventing or reducing the intensity of water or air erosion and of negative phenomena that these entail;
- encouraging the formation of hydrostable structural aggregates to improve soil permeability, aero-hydric system, water infiltration, with beneficial effects on water retainment in soil and mitigation of negative effects of prolonged drought in vegetation season;
- modifying mobility and accesibility of heavy metals in polutted / contamined soils to plants. This effect could be used in the case of soils polluted with heavy metals or polluted areas near metallurgical plants.

The main methods recommended in polluted soil remediation are: stabilization, setting up protection barriers, thermal and microbiological depollution techniques [2].

The main purpose of research consists in improving soil structure on the surface of the germinative bed with multicomponent biopolymer systems and thus ensuring better conditions for plant emergence, growth and development, particularly in species where the seed is introduced in the soil at shallow depth (up to 4 cm) and the use of structurally stabilized soil. The efficiency of using fertilizers depends not only on soil composition, but also on nutrition particularities of agricultural plants [3].

Regarding plant crops in the experimental field, it is considered that soil structure improvement positively influences the following indicators: emergence rate; final number of emerged plants; root production; increasing the plant production per hectare.

It is noted that, in order to objectively characterize soil in terms of structure conditions, a quantitative research of its stable structural composition is necessary. This is done by means of the so-called soil structural analysis, which consists in establishing stable aggregate percentages, resistant to the dispersive action of water and by means of certain qualitative characterizations based on indexes and diagrams.

The most significant issue in the study of structure is aggregate formation. The process was initially considered a simple flocculation of colloids in the soil under the influence of certain electrolytes, of calcium first of all. However, it was immediately found that the process is a lot more complex and that a simple flocculation does not provide a satisfying explanation on aggregation. Then other phenomena were introduced, proving their importance in structure formation, such as: pressure exerted on aggregates and the cementing effect of irreversible colloids, such as humus saturated with calcium.

Many researchers consider that aggregate cement is found in the organic part of colloids in the soil and prove that in intensive, strongly chemicalized agriculture, the worm population in the soil decreases, sometimes totally disappears, which has negative effects on structure formation. Restoration of worm population in the soil by human intervention is quite difficult to accomplish, since the simple introduction of such organisms in the soil is not enough, fresh organic matter, which is basic food, must be provided [4].

In this sense, it can be claimed that these multicomponent systems of protein biopolymers are favorable to the improvement of degraded soils.

MATERIAL AND METHODS

Green house (Soil Module Hall) with controlled climate conditions within National Research and Development Institute for Pedology, Agrochemistry and Environmental Protection - ICPA Bucharest.

Pots with constant volume, filled with typical cambic chernozem soil from Fundulea. Equipment used: penetrograph; penetrometer; reflectometric probe; analytical pH-meter. Protein biopolymers: BAZ - with synthetic polymer in various percentages.

Methods used for analytical characterization and research of soils - according to ICPA instructions of pedologic mapping 1982 [5].

RESULTS AND DISCUSSION

Organic biopolymers are a source of raw material for agriculture, as the composition of protein wastes provides enough nutritive elements to improve soil composition and remediate degraded soils, facilitating greenhouse and field plant growth [6].
Biopolymers have been obtained by means of an innovative enzymatic procedure of processing protein wastes resulting from leather processing, which, in combination with other polymers (polyacrylamide, acrylic polymer, maleic polymer, cellulose, starch etc.) can be used to remediate degraded/eroded soils and for greenhouse and field plant growth. Pelt wastes have been taken from the SC Pielorex tannery in Jilava - Ilfov County.

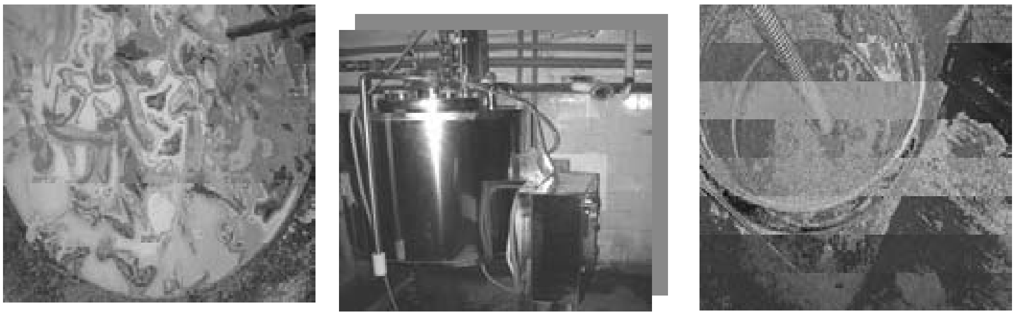

Fig. 1. Leather wastes; enzymatic hydrolysis

Fig. 2. Pots in the Soil Module Hall (ICPA green house)

In INCDTP Division: ICPI Bucharest, the BAZ (multicomponent biopolymeric systems) biofertilizers have been obtained which have been subsequently tested and experimented by ICPA - Bucharest in terms of their effect on soil structure [7].

The scientific paper presents the action of BAZ 50 biofertilizer in order to improve the structure of typical cambic soil Fundulea (with low organic substance content) under "greenhouse" conditions [8].
The morphological and chemical characteristics of typical cambic chernozem soil from Fundulea are presented below:

Name: Cambic chernozem - Fundulea
Location: The Romanian Plain, ICCPT Fundulea.
Pedogenetic conditions
Relief: plain, flat, relatively horizontal surface.
Absolute altitude: 65.3 m.
Parental material: loess deposits.
Groundwater depth: >8 m.
Natural global drainage: excessive.
Bioclimatic subarea: steppe.

Morphological Characterization of Soil Profile

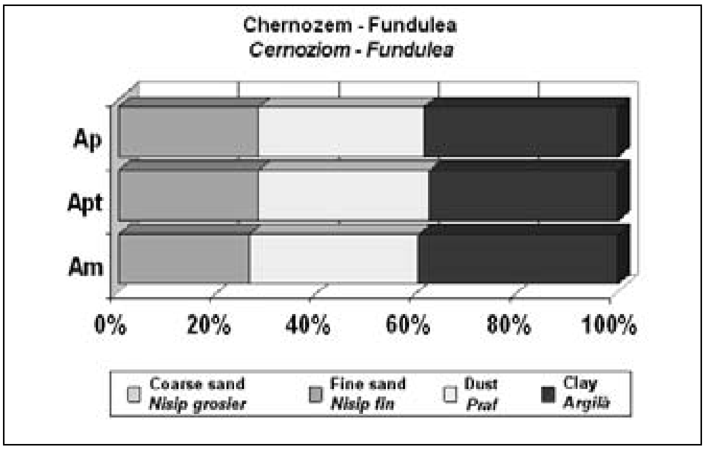

Fig. 3. Granulometry of cambic chernozem from Fundulea

Analytical data (Figure 3) regarding granulometric composition highlights the following contents of granulometric fractions: clay (<0.002 mm) values range between 37.8-40.0%. Dust content has a relatively uniform distribution, its values oscillate from 33.1 to 33.8%. Fine sand content has lower values (26.1-28.1%) than dust and has the same profile distribution. In terms of texture, this soil falls within the category of clayish-dusty clay soils.
In a soil with relatively low clay content and weak acid reaction (pH has values of 6.3-6.8), the humus quantity is low (2.4-3%) - Figure 4.

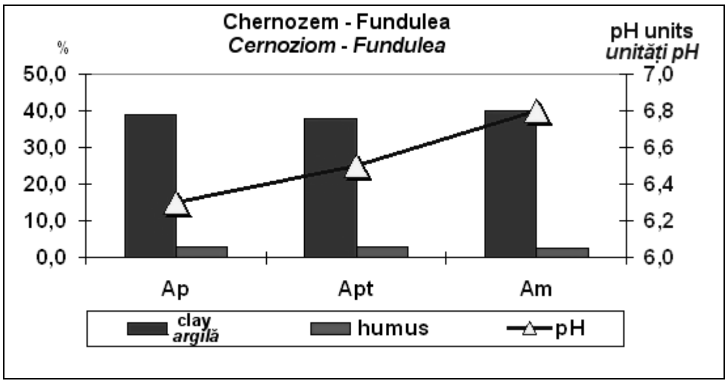

Fig. 4. Physical-chemical characteristics of cambic chernozem from Fundulea

In the development area of agricultural plant roots, the supply of total nitrogen is medium (Figure 5). The supply of mobile phosphorus is very low on the surface and low-medium everywhere else, and that of mobile potassium is low.

Table 1

Chemical properties of typical cambic chernozem - Fundulea

Horizon	UM	Ap	Aph
Horizon depth	cm	0-18	18-30
Humus (C x 1.72)	%	3.0	3.0
Total N	%	0.179	0.169
C : N	-	11.4	11.8
$CaCO_3$	%	0.0	0.0
pH (in H_2O)	pH unit	6.3	6.5
T	me/100g	21.1	21.3
$V_{8.3}$	%(T=100)	89.1	88.7
Total phosphorus (AL)	ppm	28	14
Mobile potassium	ppm	98	87

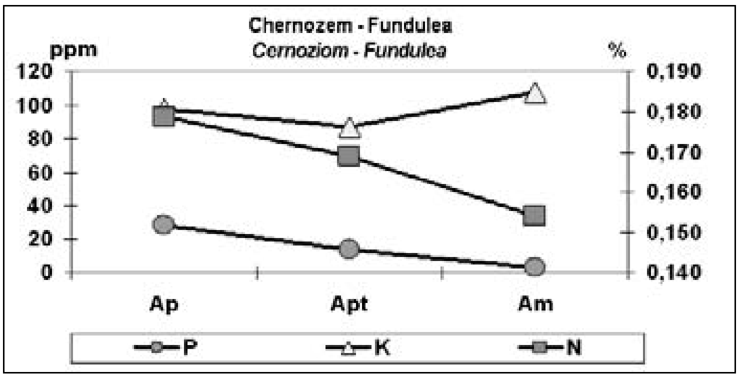

Fig. 5. The N, P supply of cambic chernozem from Fundulea

Results Obtained in the Greenhouse

Hydrostability

Regarding hydrostable macroaggregate content in the soil, laboratory analyses and determinations have highlighted the positive effect of the treatment applied with BAZ 50 biopolymer. Thus in the 0-10 cm layer, soil hydrostability of the control variant was 2-4% throughout the experimental cycle, and of the variant treated with BAZ 50 biopolymer ranged between 58 and 76% (at a concentration of 0.1% and 0.2% respectively).

In conclusion, treating typical cambic chernozem soil from Fundulea in pots with BAZ 50 biopolymer suspensions has contributed to the increase of hydrostable magroaggregate content and as far as the residual effect of treatment on hydrostability is concerned, results obtained emphasize a high content of hydrostable macroaggregates throughout experiments.

Dispersion

Regarding the effect of BAZ 50 biopolymer on the dispersion (percentage content of hydrostable microstructural elements with the diameter smaller than 0.01 mm) data obtained through laboratory analyses highlight the fact that the treated soil has lower dispersion values than the untreated soil.

Analyzing the results obtained on the soil from the 0-10 cm layer, the following are found: in the variants of treating soil on the 0-10 cm layer, the dispersion was 11.1% in the control variant, 4.2-5.3% in the treatment with BAZ 50 biopolymer in concentration of 0.1 and 0.2%. These values have clearly highlighted that application of treatment with biopolymers has led to the reduction of fine particles in the soil, namely microstructural elements with the diameter smaller than 0.01 mm. The statistic calculation emphasizes a significative difference between the variants with treated soil and the control variant with untreated soil.

Structural Instability

Structural instability expressed by a synthetic index comprising both macrostructural and microstructural data highlights the positive influence of the treatment with protein biopolymers on the structure of typical cambic chernozem from Fundulea. Analyzing data on the soil in the 0-10 cm layer, it is found that the structural instability index was 5.55 in the control variant and 0.05-0.06 in the variants treated with BAZ 50 biopolymer.

Bulk Density

Regarding soil settlement in the 0-10 cm layer, analytical data characterize bulk density as being low (1.20-1.23 g/cmc) in the control variant and extremely low (0.96-1.05 g/cm³) in variants of treating soil with suspensions of BAZ 50 biopolymer. The statistic calculation highlights a significant difference.

In conclusion, applying BAZ 50 biopolymer to improve the structure of cambic chernozem in pots has led to the improvement of settlement. Most often, the values of bulk density of the treated soil were significantly lower than the ones recorded for the untreated soil (control).

Resistance to Penetration

The analysis of laboratory determination results pn the influence of improving the structure of cambic chernozem in pots on the resistance to penetration highlights the positive effect of the treatment with BAZ 50 biopolymer. In the case of 0-10 cm layer soil, resistance to penetration was estimated as medium (approx. 32 kgf/cm²) in control and very low (7-10 kgf/cm²) in the treated variants. Statistically, the difference is significant.

Saturated Hydraulic Conductivity

Regarding soil permeability in pots, in the 0-10 cm layer, the analysis of results obtained in the laboratory highlights the positive effect of structure improvement on saturated hydraulic conductivity.

Thus permeability was moderate (0.01-0.05 log.mm-h) in the control and very high (2.27-2.66 log.mm-h) in the variants of soil treated with suspensions (0.1-0.2%) of BAZ 50 biopolymer, the difference being significant both between treated variants and particularly compared to the control.

Total Porosity

The results of laboratory analyses and determinations regarding total porosity in the 0-10 cm layer prove that total porosity was very high (58-59%) in the untreated soil from the control variant and extremely high (65-69%) in the soil treated with BAZ 50 biopolymer suspension.

CONCLUSIONS

1. Biopolymers have been obtained by means of an innovative enzymatic procedure of protein waste processing resulting from leather processing, in combination with other synthetic polymers (polyacrylamide, acrylic polymer, maleic polymer, celulose, starch, etc.).
2. The analysis of results from the determinations carried out in the Soil Module Hall (green house) regarding the effect of BAZ 50 biofertilizer (concentration 0.1-0.2%) on the improvement of cambic chernozem structure in pots.
3. Thus, the positive effect of the biopolymer was highlighted on hydrostability, dispersion, structural instability, saturated hydraulic conductivity, resistance to penetration and total porosity of cambic chernozem soil from Fundulea.

4. In conclusion, multicomponent biopolymer systems can be successfully used to remediate degraded/eroded soils and to enhance greenhouse and field plant growth.

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