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TESTING KINETIC OF NUTRIENTS RELEASE FROM COMPLEX MINERAL FERTILIZERS COATED WITH CO-POLYESTER FILMS FROM PET WASTE RECYCLING AND EFFECT ON SOIL CHEMICAL PROPERTIES

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Abstract

The paper presents researches carried out in order to test complex mineral fertilizers coated with biodegradable co-polyester films using as raw material the polyethylene terephthalate (PET) waste, such as plastic bottles for food. Achieving of biodegradable coatings, based on polyethylene terephthalate, requires modifying the chemical structure of aromatic polyester (PET) with dicarboxylic acids (aromatic and / or aliphatic), and / or other polyols, to create a biodegradable capsule for prolonged release mineral fertilizers. In order to highlight capacity of complex mineral fertilizers coated with co-polyester films, to releasing nutrients in the soil in an extended time period, unlike common complex mineral fertilizers, a green house experiment was organized. Soil material used was collected from two contrasting soil types in terms of physico-chemical characteristics, namely Luvic Phaeozems, and Calcaric Fluvisols. The experimental variants were set up in vegetation pots of about 20 kg soils / pot capacity, in which fertilizer materials were introduced, namely co-polyester films coated complex mineral fertilizers ($N_{15}P_{15}K_{15}$) and regular granular complex mineral fertilizers. The crop was very early PR39D81 hybrid corn with excellent resistance to drought (hybrids belonging to the group FAO 200). Soil samples were collected during the plant vegetation, especially in the flowering stage and maturity stage (at harvest) for analyzing of the main chemical properties: soil reaction, organic carbon content, humus content, total nitrogen and nitrates contents, mobile phosphorus and potassium content in different fertilization variants. Data obtained in this experiment have been shown that the use of mineral fertilizers coated with co-polyester films in the proposed formula was beneficial for ensuring soil nutrients over a longer time, and thus, to be available to plants along the most vegetation period.

Keywords: *co-polyester films, mineral fertilizers, polyethylene terephthalate, slow-release, soil.*

INTRODUCTION

Replacement of natural resource use by the appearance and development of plastics, lightweight and very resistant, has become one of the most serious environmental problems because of the durability of these materials, which leads to accumulation of huge amounts of waste. In this case, nature, single, can not solve the problem, its huge self-cleaning capacity is no longer useful because most waste plastics can not be degraded by microorganisms.

In the middle of the 9th decade of last century, worldwide production of polymer materials was estimated to be approximately 150 million, with an average yearly consumption of 80–100 kg per capita in industrialized countries [17, 21]. An estimated 40% of this total production has been discarded into landfills [16]. In addition, plastic products and derivatives are now ubiquitous in the natural environment, being present even in marine environments, including sediments [6, 8, 18, 19, 22].

Recycling as an alternative to storage is limited by high costs included, and potential hazards such as dioxin emissions from incineration [13, 11].

Aromatic polyesters such as polyethylene terephthalate, so-called PET shows excellent properties, which caused him to be marketed worldwide, often as packaging for liquids. However, until now, these polymers are considered resistant to microbial attack, so there is biodegradable, which is a huge disadvantage [9, 1, 10]. Starting from a desire to meet both biodegradability and superior properties of plastic materials, tests were performed on biodegradability co polyester monomers containing both aliphatic and aromatic [24]. Biodegradability of a plastic is implying the possibilities of living organisms to use it as a food source, by transforming its chemical structure within a reasonable period of time. The organisms which having this metabolic ability are microorganisms. Primary (or partial) biodegradability is altering the chemical structure resulting in loss of specific properties of polymers while the final (or total) biodegradability is total mineralization and assimilation of the resulting material by microorganisms [4, 3, 5]. The material is fully degraded by microorganisms to produce carbon dioxide or methane, water, mineral salts and biomass [15, 2]. The time period involved is usually several weeks to several months.

Because of the insolubility and large size of polymers molecules, microorganisms are unable to transport polymeric material directly to their cellular structure, where most biochemical processes take place. Thus, microorganisms must first release extracellular enzymes that catalyze the depolymerization of polymers outside the cell walls. If and when the molar mass of polymer is reduced enough to generate water-soluble intermediates, they can be carried inside the organisms, and placed in appropriate metabolic circuit.

The physicochemical flexibility of branched polyesters achieved through simple modification of the polymer systems, making them very usefully for the development of a variety of drug delivery vehicles in biomedical industry. The polymers' modular design is advantageous for the encapsulation of a wide range of drug compounds [7].

To avoid problems caused by dissolving of fertilizers in soil moisture at a speed higher than its absorption in the plant, many types of slow-release active substance fertilizers were designed. One method to obtain such products involves creation of "core / shell" type microcapsule, where *shell* consists in a polymeric film with low water permeability and the *core* is the active substances. If the polymer used for encapsulation is biodegradable, fertilizers are released slowly as a result of polymeric film biodegradation [11].

To obtain biodegradable coating materials, from polyethylene terephthalate, was performed modifying of the chemical structure of aromatic polyester (PET) by including of dicarboxylic acids and / or other polyols, thus resulting a co polyester structure. This co-polyester presents molecular weight high enough to ensure formation of a flexible and resistant to moisture continuous coating film proper for producing encapsulated fertilizers; able to provide controlled release of fertilizers, mainly by biodegradation, and which can being decayed to a convenient and measurable period of time under the influence of environmental factors.

Soil parameters such as humidity, temperature, pH, salinity, presence or absence of oxygen and nutrient supply level exerts a powerful effect on microbial degradation of polymers, so these conditions must be taken into account when testing biodegradability of polymers .

The most common methods of testing the biodegradability of polymers in the soil are: soil burial test, the so-called "controlled composting test" [14, 20, 22], and spreading the field simulation test "landfill" [12].

MATERIAL AND METHOD

In order to highlight capacity of complex mineral fertilizers coated with co-polyester films, to releasing nutrients in the soil in an extended time period, unlike common complex mineral fertilizers, a green house experiment was organized, using soil material collected from two contrasting soil types in terms of physical-chemical characteristics, especially argyle content, namely Luvic Phaeozems, and Calcaric Fluvisols.

Experiment carried out in greenhouse, in vegetation pots with capacity of 20 kg of soil material / pot, with 5 repetitions for each variant, with those two different types of fertilizers: regular complex mineral fertilizers ($N_{15}P_{15}K_{15}$), and complex mineral fertilizers ($N_{15}P_{15}K_{15}$) coated with co-polyesters films, according to following experimental scheme:

Treatment code	Soil type	Treatment
V1	Luvic Phaeozems	Control - unfertilized
V2		Regular complex mineral fertilizers ($N_{15}P_{15}K_{15}$)
V3		Complex mineral fertilizers ($N_{15}P_{15}K_{15}$) coated with co-polyesters films
V4	Calcaric Fluvisols	Control - unfertilized
V5		Regular complex mineral fertilizers ($N_{15}P_{15}K_{15}$)
V6		Complex mineral fertilizers ($N_{15}P_{15}K_{15}$) coated with co-polyesters films

The crop was very early PR39D81 hybrid corn with excellent resistance to drought (hybrids belonging to the group FAO 200).
During the plants vegetation, especially in the flowering and maturity (at harvest) stages, soil samples were collected and analyzed in the laboratory to determine the reaction (pH in aqueous solution), total nitrogen content by Kjeldahl method, accessible phosphorus and potassium contents (soluble in the ammonium-acetate- lactate solution at pH 3.7) by UVIS spectrometry (phosphorous) and flame-photometry (potassium), and the nitrates content in order to establish how are released the minerals elements from the four types of granular fertilizer coated with co polyesters films. Analytical methods are in accordance with national (STAS) and international (ISO) standards. Data were statistically processed using standard analysis of variance (ANOVA).

RESULTS AND DISCUSSIONS

Soil reaction was not influenced by the type of fertilizer applied, differences in values being generated by the different native reactions of two soils used for experimentation (Fig. 1). The importance of this aspect is that the obtained data prove that the co polyester film used for covering the complex mineral fertilizers does not change the soil reaction, without having to impose any limitations in the utilization of this type of fertilizer for strongly acidic or alkaline soils.

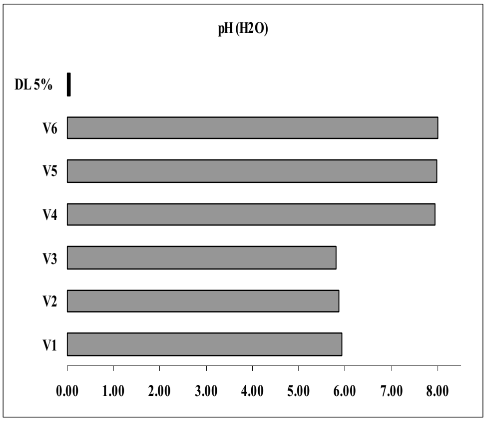

Fig. 1. Effect of fertilizer type on soil reaction

Humus content did not present variation in the experimental variants, except those generated by different native qualities of the two types of soil used, Luvic Phaeozems having, naturally, a higher organic matter content as compared with the Calcaric Fluvisols, soil poor in clay and with a high sand content (Fig. 2).

Total nitrogen content. Besides the inherent differences existing between the two soil types, the total nitrogen content in Luvic Phaeozems fertilized with complex mineral fertilizers coated with co polyester films was significantly reduced as compared with the variant in which regular fertilizers have been applied (Fig. 3). The analysis results have shown that at flowering stage of maize plants, nitrogen from the mineral fertilizers coated with co polyester film not been fully released, remaining still a reserve available for further plant vegetation period.

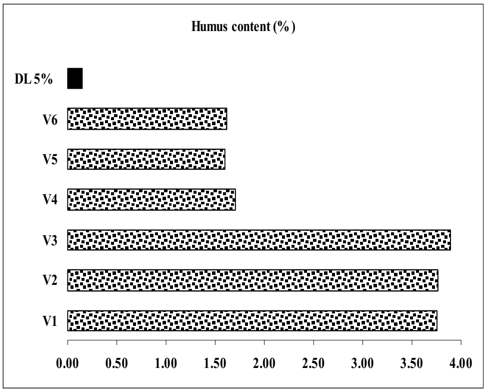

Fig. 2. Effect of fertilizer type on soil humus content

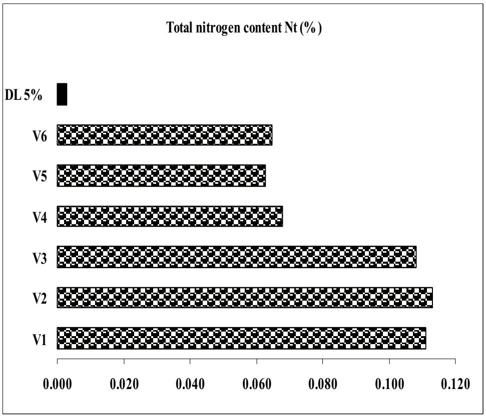

Fig. 3. Effect of fertilizer type on soil total nitrogen content

The nitrates content, nitrogen chemical form most useful for plant nutrition, shows significantly lower values in fertilized variants, as compared with the control, in Luvic Phaeozems.

It was noticed a significant difference between the two types of applied fertilizers, thus in the variant with complex mineral fertilizers coated with co polyester films, nitrates content reported was lower (Fig. 4).

The same situation has been repeated in variants carried out on the second soil type, Calcaric Fluvisols respectively.

Considering that the soil analysis were performed in a stage of high metabolic activity of corn plants, in the flowering period, the explanation may be that in the mineral fertilized variants, plants have had a greater capacity to absorb this nutrient from soil, hypothesis that can be confirmed by their phenological aspect. In the mineral fertilized variants in both fertilization and soil types, the plants were clearly more vigorous.

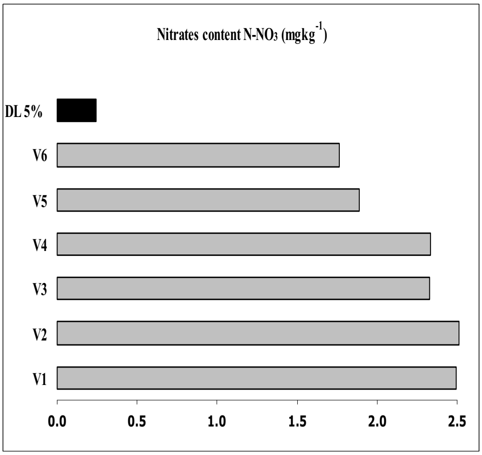

Fig. 4. Effect of fertilizer type on soil nitrates

Mobile phosphorus content, chemical form available for the plant nutrition, shows very significant differences between variants (Fig. 5).

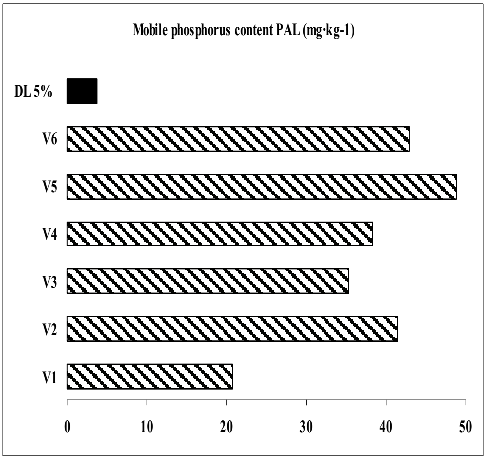

Fig. 5. Effect of fertilizer type on mobile phosphorus content

As it was expected, for the both types of soil, mobile phosphorus content, determined in mineral fertilized variants are higher than control variants, applied phosphorus being found, but, also for the both soils, the contents are significantly higher in variants fertilized with regular complex mineral fertilizer, compared with those fertilized with mineral fertilizers coated with co polyester films

The data clearly show that the time required for release of this chemical element from the co-polyester capsule is prolonged, compared with the period recorded for nitrogen releasing.

Mobile potassium content presented a dynamic, somewhat similar to that recorded in cases of total nitrogen and nitrates contents, shows significantly lower values in fertilized variants, as compared with the control, in Luvic Phaeozems. That means the corn plants more efficiently used this nutrient from fertilized variants, moreover, entailing even natural reserve of soil potassium, especially in Luvic Phaeozems case (Fig. 6).

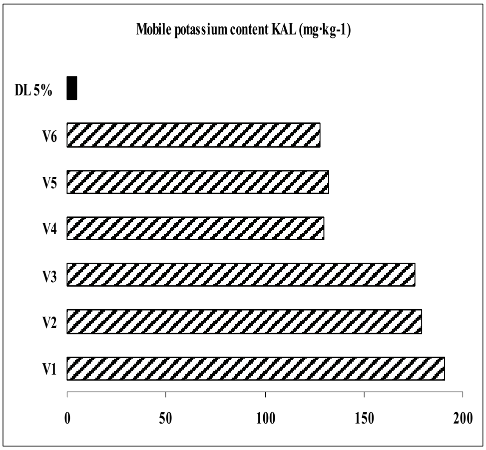

Fig. 6. Effect of fertilizer type on mobile potassium content

CONCLUSIONS

Experimental data clearly shows the beneficial effects of complex mineral fertilizers with NPK application, both in regular formula, but also in that of mineral fertilizers coated with co polyester films.

Data obtained in this experiment have shown that the effects generated by the use of complex mineral fertilizers coated with co polyester films, in the formula proposed in this research, have been beneficial to provide soil nutrients over a longer period to be available to plants.

Use of complex mineral fertilizers coated with co polyester films in formula proposed in this research did not induced toxicity aspects for soil microorganisms which would implicitly leads to breakdown of the bio-geo-chemical circuits, which are the foundation of soil fertility.

Our research highlighted that the use of PET waste for production of co polyester films with applicability in production of complex mineral fertilizers, in prolonged release formulation, is a real and extremely useful possibility for recycling of this waste which has been accumulated in the environment in huge quantities.

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