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Microencapsulated fertilizers for improvement of plant nutrition

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Abstract: Given the need to reduce the impact of the use of chemical fertilizers on the quality of food crop production, it is necessary to develop fertilizer formulations enabling the gradual and controlled release of the active substance, which could be achieved by encapsulation, thereby allowing its almost complete metabolization by plants. The study reported herein was intended to test such fertilizer compositions with controlled release, achieved by encapsulation in polymeric structures, by monitoring the biological activity of the new products, using maize and sunflower crops as the target plants, *i.e.*, crops having a major impact in the agricultural sector. To achieve this objective, solid microstructures were obtained, which allowed, on one hand, the incorporation of the fertilizing composition and, on the other, the controlled release of the active components over a period of time chosen so that advanced absorption in the plants could occur. Based on the presented findings, the tested fertilizers could ensure high quality fertilization in terms of a greater degree of nutrient recovery, lower doses without reducing plant productivity and reduced chemical pollution of soil.

Keywords: fertilizer; maize; sunflower; production increase; controlled release.

INTRODUCTION

The use of excessive amounts of mineral fertilizers leads inevitably to the emergence of crops containing large amounts of chemicals from the fertilizers, ultimately reaching the food chain and affecting the health of the consumers, thus having an extremely negative impact on the environment.[1] Given the need to reduce the impact of the use of chemical fertilizers on the quality of food crop production, it is therefore necessary to develop fertilizing formulation with gra-

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dual and controlled release of the active substance, *e.g.*, by encapsulation, so that the fertilizer could be almost completely metabolized by the plants.

Due to the many advantages of the encapsulation process, the field has grown exponentially in recent years. The classes of compounds considered in this technique are extremely varied, ranging from medications,[2] food ingredients[3] and enzyme systems[4] to the encapsulation of highly toxic chemical residues, for their detoxification.[5] Thus, a number of studies have been performed worldwide regarding the microencapsulation of mineral fertilizers, in which various techniques were employed in order to obtain a controlled release fertilizer, thereby avoiding overdosing with the accompanying negative effects.[6,7]

The present paper intends to characterize such fertilizer compositions with controlled release, achieved by encapsulation in polymeric structures, by testing the biological activity of the new products, using maize and sunflower crops as target plants, crops with a major impact in the agricultural sector. To achieve this objective, solid microstructures were obtained to allow, on one hand, the incurporation of the fertilizing composition and, on the other, the controlled release of the active components in a period of time chosen so that advanced absorption in the plants could occur.[8]

EXPERIMENTAL

Materials

The fertilizers intended for use in the biological efficiency tests were microencapsulated urea; 1–1–0 NPK (nitrogen–phosphorous–potassium) complex; 1–1–1 NPK complex; 2–1–1 NPK complex. The methods for the synthesis of the proposed structures were presented in previous papers.[9–11]

The raw materials used for the fertilizers formulation were: urea (granules, SC Donau Chem SRL Turnu Magurele, Romania); formaldehyde aqueous solution (37 %, SC Chimreactiv SRL Bucharest, Romania); paraformaldehyde (solid, containing minimum 98 % formaldehyde, BDH Chemicals Ltd., UK); monoammonium phosphate (SC UTCHIM SRL Rm. Valcea, Romania); potassium chloride (SC Chimreactiv SRL Bucharest, Romania); phosphoric acid aqueous solution (85 % SC Chimreactiv SRL Bucharest, Romania); potassium hydroxide (aqueous standard solution, concentration 40±1 %); *n*-hexane (Vega Ploiesti, Romania); sodium tetraphenylborate (Fluka). All the materials are commercially available and were used as received, with no further purification.

Methods

The process of determining the degree of leaching of fertilizer on a column with sandy soil consisted of the following:

– The use of an installation consisting of columns of the following dimensions: I = 60 cm. d = 20 cm and 314 cm^2 column inner area, having a vessel at the bottom for collection of the solution.

– Incorporation at the top of the column filled with sand to a depth of 20 cm at a dose of 20 g fertilizer.

– Filling the columns with sandy soil with the following characteristics: 0.2 % humus content; total nitrogen 0.3 %; phosphorus <15 mg kg^{-1}; mobile potassium: 20 mg kg^{-1}; pH 6.5.

Given the humus content, the N/P/K content and the soil reaction as factors influencing plant nutrition, it was established that the testing of the microencapsulated and coated fertilizers must be realized on psamosoil (sandy soil) with a very low content of humus, nutrients and with a neutral reaction. With high permeability, very low content of humus and nutrients, sandy soil meets the optimum qualities to determine the leaching of fertilizers.

Regarding leaching producing irrigation, from the maximum standards set out in the literature for a main culture, *i.e.*, 4000–5000 m^3 water ha^{-1} (400–500 L m^{-2}) over 6–10 waterings of 600–700 m^3 water ha^{-1} (60–70 L m^{-2}) each, was considered effective and justified the application in columns of 8 waterings of 60 litres volume, every 8 days.[12] For irrigation, potable water from Bucharest was used. Product quantity – 20 g, nutrient content (**NPK**): **100** – 6.76 g N_t (33.82 %); **110** – 4.094 g N_t (20.47 %), 4.306 g P_2O_5 (21.53 %); **111** – 2.942 g N_t (14.71 %), 2.833 g P_2O_5 (14.16 %), 2.705 g K_2O (13.52 %); **211** – 4.336 g N_t (21.68 %), 2.417 g P_2O_5 (12.08 %), 2.387 g K_2O (11.93 %).

At the end of each eight-day cycle, the percolated water from the sand column was measured and analysed and the following standardized analyses were performed: determination of nitrogen by mineralization and distillation (Kjeldahl method); determination of phosphorus by the quinoline phosphomolybdate method; determination of potassium by the tetraphenylborate method [13]

Water leaching tests were performed and the results, from the point of view of the influence on plant nutrition, were compared with those obtained using classic fertilizers, commercial and non-encapsulated in a polymeric matrix.

The experimentation was conducted in a greenhouse in Mitscherlich vegetation vessels with 20 kg of soil, vermic chernozem, which is widely spread on the Romanian plain and various important areas on the Barlad Plateau, Transylvania and the Banat plain.

Chemical analysis (Table I) showed that the soil on which the tests were organized was fertile.

TABLE I. Chemical analysis of vermic chernozem; N_t – total nitrogen; P_t – total phosphorus; P_{AL} – phosphorus assimilable from the soil; K_{AL} –potassium assimilable from the soil

Soil type	Component						
	Humus	N_t	P_t	P_{AL}	K_{AL}	Ca	Mg
	%			mg kg^{-1}			
Vermic chernozem	3.5	0.18	0.015	35	56	180	65

The soil was introduced into the vegetation vessels (20 kg per vessel) and well levelled. Each variant was realized in three replications. Fertilization was performed pre-sowing by application of the product in the upper third of the soil in the vessel.

For the maize crop, the Talman simple hybrid was used, while for the sunflower, the Favourite variety was introduced. Maintenance of the crops was specific for the two species. Crop watering was ensured permanently at 70 % of field capacity of the soil. Harvesting was performed at crop maturity. The experimental results were expressed as the main product increase (maize grains, sunflower seeds) in g per vessel, % and in product grams per gram of active substance fertilizer (AS). The dose of fertilizer used was 20 g fertilizer per vessel.

RESULTS AND DISCUSSIONS

The main quality of microencapsulated fertilizers is the release of nutrients by slow solubilisation, over a period of time significantly longer than non-encapsulated mineral fertilizers, which are water soluble. Thus, the plants benefited from the improved nutrition through these fertilizers for a longer period and which ensured higher yields due to the higher ratio of nutrients used.[9]

Mineral fertilizers selected to be microencapsulated, either with one element (ureic nitrogen, for urea), two elements (nitrogen and phosphorus), or all three essential nutrients (nitrogen. phosphorus and potassium), once incorporated into the soil fill the nutrients reserve at optimal levels for the crop. The amounts of nutrients incorporated in microcapsules are leached (those with nitrogen), downgraded by reaction with the in soil existing calcium (those with phosphorus), respectively degraded in smaller amounts. Thus, fertilization doses can be reduced to a certain degree without reducing plant productivity and the fertility of the soil, thereby substantially reducing chemical pollution.[14]

Since this type of fertilizer has as its main feature the slow and controlled release of nutrients over time, thus preventing their leaching from the soil layer down to a depth of 60 cm, where the roots of most plant are widespread, the preliminary tests involved the characterization of each type of fertilizer obtained, in dependence on the leaching degree in an intensively pluviometric percolation regime.

Preliminary tests consisted of determining the leaching degree of the nutrient constituents (N_2, P_2O_5 and K_2O). Experimental results are given in Table II.

TABLE II. Leaching degree of the nutrient constituents

Percolation	Fertilizer (N:P:K)								
	1:0:0	1:1:0		1:1:1			2:1:1		
	N	N	P	N	P	K	N	P	K
P1	0.630	0.360	0.145	0.420	0.0192	0.0584	0.3944	0.0752	0.06
P2	0.595	0.345	0.122	0.2744	0.0968	0.0816	0.4248	0.1328	0.1152
P3	0.313	0.220	0.109	0.1144	0.1408	0.1168	0.2136	0.176	0.0848
P4	0.165	0.168	0.098	0.0792	0.1256	0.1112	0.170	0.176	0.068
P5	0.036	0.085	0.09	0.0352	0.104	0.064	0.1448	0.1136	0.0325
P6	0.015	0.070	0.086	0.0184	0.0768	0.0448	0.090	0.0696	0.028
P7	0.015	0.065	0.085	0.0184	0.0744	0.0408	0.080	0.0656	0.028
P8	0.014	0.040	0.083	0.0168	0.0664	0.0336	0.0752	0.06	0.0248
Total	1.783 (26.4 %)	1.353 (33.0 %)	0.8185 (19.0 %)	0.9768 (33.2 %)	0.704 (24.8 %)	0.5512 (19.4 %)	1.5928 (36.7 %)	0.8688 (35.9 %)	0.4413 (18.5%)

From Table II, it could be seen that the forms of NPK fertilizer NPK 110 and 111 provide a uniform release over time of the macronutrient content (compared to the original content), while presenting a very good leaching resistance ("slow--release" activity), which recommended these formulations to be considered for future work.

The results of the leaching degree tests proved that the nitrogen incorporated into microencapsulated fertilizers was released slowly, over a long period, providing improved nutrition and reduction of pollution. Phosphorus and nitrogen applied simultaneously had positive influences on the root surface and on the absorption process due to changes in the ratios between the ions present in the layer adjacent to the root surface. Nitrogen also promoted the release of phosphorus from combinations of energy transfer, increasing its effect in the cells of the plant root. Phosphorus affects nitrogen uptake by increasing root respiration.[15–17]

The test results showed the effectiveness of microencapsulation in prolonged maintenance of the solubility of phosphorus (P–$H_2PO_4^-$), which leached for up to 64 days compared to the downgraded ($H_2PO_4^-$), which occurred within a few days after incorporation into the soil.

Romanian soils are well supplied with assimilable potassium. Fertilizers containing this element can be used on sandy and luvic soils, or eroded as well as on other well-supplied soils under intensive cultivation of agricultural plants, fertilized with high doses of fertilizers. Microencapsulated potassium fertilizers are of interest for high-dose intensive fertilization.

Conventional, commercial fertilizers ensure the production increases given in Table III.

TABLE III. Production increases (%) of maize and sunflower ensured by fertilizers

Culture	Urea	NPK 110	NPK 111	NPK 211
Maize	10–12[a]	70–75[a]	Max. 40[b]	180–190[a]
Sun flower	15–17[a]	85–90[a]		150–160[a]

[a]source – field tests conducted using classic, commercial products, of the same compositions as those used in this study under the same conditions as those used for testing the developed fertilizers; [b]NPK 111 (15 % nitrogen, 15 % phosphorus, 15 % potassium), Azomures commercial product, the manufacturers guaranteed maximum increase

It could be seen that the smallest increases are provided by urea, which is only a source of nitrogen, and does not provide phosphorus and potassium, required by plants. On the other hand, the higher increases were obtained with conventional fertilizers, NPK 211. The disadvantage of this formulation in comparison to the NPK 111 is the higher cost of manufacturing. In addition, these increases are obtained with greater amounts of fertilizers, as several side fertilizations are necessary in order to compensate the losses caused by physical or chemical processes in the soil.

The efficiency of microencapsulated fertilizer on maize is presented in Table IV. The production increase relative to the total amount of active substance (AS) was differentiated according to the presence of the fertilizer components: N, NP and NPK, as well as the relationship between the elements N, P and K contained in the ternary fertilizers. The lowest growth increase (42.38 %) compared to the control unfertilized samples, was recorded for microencapsulated urea, but the increase was substantially higher (91.62 %) with the binary NP fertilizer (110).

This increase is due to the essential effects of nitrogen and phosphorus applied in combination on plant nutrition. The production increase obtained with the ternary complex fertilizer NPK 111 was superior to that of the binary one, 136.6 % higher compared to the control.

TABLE IV. Efficiency of microencapsulated fertilizer on maize

No.	Fertilizer	Quantity g per vessel	Grain production g per vessel	Increase		Production increase
				g per vessel	%	g per g of fertilizer
1	Unfertilized	–	51.2	–	100.00	–
2	100	6.76	72.9	21.7	142.38	2.89
3	110	8.40	98.11	46.91	191.62	5.58
4	211	9.14	104.86	53.66	204.80	5.87
5	111	8.48	121.14	69.94	236.60	8.24

Production increases presented with N, NP and NPK minimum dose of 6.76 to 9.14 g AS per vessel, certified that, to ensure optimum plant nutrition for intensive agriculture, all three elements are required, even for fertile soils.

Significantly greater production increases were obtained with NP and NPK complex fertilizers containing these elements in different ratios.

Thus, the microencapsulated NPK 110 complex fertilizer achieved an increase of 91.62 %, *i.e.*, 5.58 g grains per g of fertilizer, compared with the unfertilized control sample.

The use of microencapsulated NPK 111 complex fertilizer was favourable for maize, resulting in an increase of 136.60 %, *i.e.*, 8.24 g grains per g fertilizer, compared to the unfertilized control.

For urea the lowest production increase was recorded, as the plant assimilates nitrogen to a lesser extent in the absence of phosphorus.

In conclusion, all microencapsulated fertilizers tested led to considerable improvements in maize plant nutrition embodied in their proper vegetative development, which resulted in significant yield increases.

The effectiveness of the microencapsulated fertilizers applied to sunflower is presented in Table V.

TABLE V. Effectiveness of the microencapsulated fertilizers applied to sunflower

No.	Fertilizer	Quantity g per vessel	Grain production g per vessel	Increase		Production increase
				g per vessel	%	g increase per g of fertilizer
1	Unfertilized	–	27.3	–	100.00	–
2	100	7.12	46.13	18.83	168.97	2.64
3	110	8.40	66.98	39.68	245.34	4.72
4	211	9.14	69.4	42.1	254.21	4.60
5	111	8.48	78.8	51.5	288.64	6.07

Microencapsulated urea increased the production of seeds by 68.97 % (2.64 g seeds increase per g fertilizer). The binary complex NPK 110 fertilizer enhanced the yield by 145.34 % (4.72 g seeds per g fertilizer), while with the complex NPK 211 fertilizer the increase was 154.21 % (4.60 g seeds per g fertilizer). The ratio of the NPK complex fertilizers was also important for seed production. The complex NPK 111 fertilizer led to a yield increase of 188.64 % (6.07 g seeds per g fertilizer). The achieved production increases, lower than in the case of maize, could be explained by the fact that sunflower responded best to the NPK 111 fertilizer, while maize is a higher consumer of nutrients.

In conclusion, it could be stated that the microencapsulated fertilizers provided for significant production increases for sunflower.

Table VI presents a summary of Tables IV and V, and contains specific production increases (production increase in grams, compared to the amount of fertilizer used), obtained for both maize and sunflower crops.

TABLE VI. Specific production obtained for both maize and sunflower crops

No.	Fertilizer	Specific production increase g increase per g of fertilizer		Average production increase g increase per g of fertilizer
		Maize	Sunflower	
1	Unfertilized	–	–	
2	Microencapsulated urea	2.89	2.64	2.76
3	NPK 110	5.58	4.72	5.15
4	NPK 211	5.87	4.60	5.24
5	NPK 111	8.24	6.07	7.16

It should be noted that for maize with microencapsulated NPK complex fertilizer, 111 was the most favourable ratio, with which there was a maximum specific increase in grain production of 8.24 g per g fertilizer compared to the unfertilized control.

For sunflower crops, the specific increase in production using microencapsulated urea was 2.64 g seed per g fertilizer.

Regarding complex NPK fertilizers with various ratios of N, P and K, specific increases in seed production are also important. The complex NPK 111 led to an increase of 6.07 g of seeds per g of fertilizer.

The average production increase was calculated as the average of the two specific production increases. The employment of microencapsulated urea generated specific production increases comparable for the two cultures at the lowest cost price (this microencapsulated fertilizer being the cheapest).

CONCLUSIONS

All microencapsulated fertilizers studied meet the physical and chemical demands that facilitate superior storage, handling and differentiated fertilization depending on the content of the active substance. All samples of the tested microencapsulated fertilizers were characterized by gradual leaching, over a significantly longer period than the non-encapsulated mineral fertilizers, thus having a significant "slow- release" activity.

From the determination of the degree of leaching of water-soluble substances embedded in microencapsulated fertilizers, it could be concluded that they were greatly reduced compared with conventional fertilizers. As a result, the employment of this type of fertilizers ensures significant reduction in chemical pollution and a much higher proportion of the nutrients are taken up by the plants.

For all investigated fertilizers, an improved resistance to leaching of the nutrients was recorded, which resulted in significantly lower leaching degree. The explanation is that in the case of these fertilizers, the release of nutrients through leaching occurs over a longer period than from conventional mineral fertilizers (non-encapsulated). Thus, the plants benefit from improved nutrition for longer periods and higher production yields are ensured due to the higher ratio of the usage of the nutrients.

By supplementing the deficient nutrients in soil, in relation to the actual plant requirements, and by the influence they exert on the dynamics of the uptake of nutrients, encapsulated mineral fertilizers are an important means for directing plant nutrition and, thereby, influencing their growth and development throughout the vegetation period. When applied together, phosphorus and nitrogen have positive effects, each influencing the uptake of the other.[15–17]

Due to microencapsulation, the nutrients undergo leaching (nitrogen) or a downgrade (phosphorus) through chemical reactions that occur in soil to a significantly smaller extent than is the case with non-encapsulated mineral fertilizers. Thus, in tests conducted for nitrogen leaching for non-encapsulated urea and ammonium nitrate, the obtained values (42.4–44.6 %) were much higher than for the encapsulated fertilizers (28.03–34.11 %).

Regarding the dynamics of phosphorus, which leaches to a much lower extent than nitrogen, but suffers a downgrade into soluble forms within a few days, microencapsulated fertilizers ensure an extension of time periods for maintaining the monophosphate form, due to the slow and gradual release during plant vegetation.

The results for the dynamics of potassium leaching show a positive influence of encapsulation on the extended dissociation of potassium ions in the fertilizers and root uptake from a soil intensively fertilized.

The production increases that were obtained with the microencapsulated fertilizers are due to the fact that, in addition to intake of nutrients, such fertilizers in the soil give rise to a series of slow and longer chemical and biological reactions (enzyme-catalysed reactions, such as the hydrolytic decomposition of urea by the enzyme urease), through which the dynamics of many substances existing in soil are also influenced. The production increases provided by the microencapsulated fertilizers in maize and sunflower grown in vermic chernozem, the soil prevalent in Romania, are high, ranging from 42.38 to 136.60 % compared to the control unfertilized maize, and between 68.97 to 188.64 % compared to the control in sunflowers. These production increases certify the superior quality of these new crop fertilizers that are to be used in sustainable agriculture, which is the main objective today.

Based on the outlined findings, these fertilizers could ensure high quality fertilization in terms of a greater degree of nutrient recovery, lower doses required to maintain high plant productivity and reduced chemical pollution of soil.

И З В О Д

ЂУБРИВА У МИКРОКАПСУЛАМА ЗА БОЉУ ИСХРАНУ БИЉАКА

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Да би се смањио утицај хемијских ђубрива на квалитет житарица за исхрану, пожељно је правити ђубрива у капсулама, у циљу постепеног и контролисаног отпуштања активних супстанци, омогућујући биљкама да их скоро у потпуности метаболишу. У овом раду су тестирана ђубрива инкапсулирана у полимерне структуре, а праћена је биолошка активност у кукурузу и сунцокрету, житарицама веома важним у пољопривреди. На основу добијених резултата, могло се закључити да се оваквим ђубривима постиже квалитетно ђубрење у смислу искористљивости хранљивих састојака, потребне су биле мање дозе ђубрива, није долазило до смањења производње житарица, а било је смањено загађење земљишта.

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