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PHOSPHATE GLASSY FERTILIZERS

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Abstract

The main goal of agricultural production should be the production of a sufficient amount of agricultural products with the least possible impact on the environment. In traditional agricultural production, to obtain a satisfactory yield, artificial fertilizers are used, which have multiple negative impacts on the environment. Glassy fertilizers are a type of fertilizer that, at least according to previous research, do not have a negative impact on the environment, and at the same time the use of these fertilizers yields no less than when using traditional fertilizers. Glassy fertilizers are fertilizers with controlled dissolution, they do not pollute groundwater or surface water, and the pH of the soil does not change with their use, by changing the composition they can adapt to the requirements of each crop individually, etc. The paper presents three phosphate glassy fertilizers of different chemical compositions, obtained at the Centre for Inorganic Technologies, ITNMS. The method of obtaining glassy fertilizers, their dissolution rates in a medium that simulates soil conditions, the changes in pH values of solutions for different dissolution times, and the effect of temperature on dissolution rates are shown. Also, the results of the influence of glass fertilizers on plant cultures in real conditions are presented.

Keywords: glassy fertilizers, phosphate, dissolution rate.

Introduction

Controlled release fertilizers (CR fertilizers) are those materials that have nutrients for the plant and can dissolve after some time from the moment of introduction into the soil (″to delay their availability″), they are available to the plant much longer than conventional fertilizers (Calabi-Floody et al, 2018). One of the groups of ecological CR fertilizers is glassy fertilizers (GF). These glasses have a polymer structure, and the glass network can be made up of one, two, or more network builders, while cations of different metals are placed in the cavities (Ersundu et al., 2022). Various macro (K, P, Mg, Ca) and micro (B, Fe, Mo, Cu, Zn, Mn) nutrients, necessary for the growth and development of plants, can be included in the composition of glass in a relatively simple way (Cacini et al, 2020). The dissolution of glass is a complex process that takes place in several stages and which, apart from the chemical composition and granulation of the glass, also depends on the temperature, pH of the solvent, time of action, etc. (external conditions). The total dissolution time can be designed to favor or inhibit one of these phases. During the growing season, plants intensively consume the components that are separated from the glass, and thus the driving force for the dissolution process increases. The solubility of glassy fertilizers can be adjusted to a certain plant culture or natural conditions (climate and soil characteristics), by changing the chemical composition and granulation of the glass (Sirotkin et al, 2012).

The use of GF in agricultural production has a positive impact on the natural environment and does not lead to a decrease in yield, they do not wash into the lower layers of the soil because the unused part of the glass remains in the upper layers of the soil, the nutrients are easily accessible, etc. (Szumera et al, 2005). Research shows that by using GF, plants get a sufficient amount of nitrogen because these glasses encourage the activity of microorganisms from the soil to bind nitrogen from the air into forms suitable for plant nutrition (Karapetyan et al, 2004).

This paper presents three phosphate GF of different chemical compositions, obtained at the Center for Inorganic Technologies, ITNMS. The method of obtaining glassy fertilizers, their dissolution rates in a medium that simulates soil conditions and the effect of temperature on dissolution rates are shown. Also, the results of the influence of glass fertilizers on plant cultures in real conditions are presented.

Materials and Methods

The appropriate glass batches compositions were prepared from reagent-grade raw materials $(NH_4)_2HPO_4$, K_2CO_3, $CaCO_3$, SiO_2, MgO, ZnO, Fe_2O_3, CuO, B_2O_3, and MnO_2 in an open porcelain crucible (the preparation of the glass batches described in the patent, number 61428 (2021)-The Intellectual Property Office of the Republic of Serbia). The glasses mixture was melted at T = 1100 °C (GF2) and 1300 °C (GF1, GF3) for t=1h in an electric furnace, and the melt was quenched on a steel plate. Powder X-ray diffraction (XRD) analysis confirmed the quenched melt to be vitreous (data not shown). The chemical composition of glass was determined by gravimetric (Si) and spectroscopic methods, *i.e.*, by AAS using a PERKIN ELMER 703 instrument (Ca, K, Mg, Cu, Zn, Fe, B-standard solutions 1000 µg/ml) and UV/VIS spectroscopy using a PHILIPS 8610 spectrophotometer (P- standard solutions 1000 µg/ml) The chemical composition of the glasses is presented in Table 1.

The chemical stability of the glasses (granulation 0.3-0.65 mm) was determined in a 2% citric acid solution (a solution that simulates the environment around plant roots) at several temperatures.

Results and discussion

Table 1. presents the analyzed composition of the glasses.

Table 1. Chemical composition of glasses

	Macronutrients			SiO_2	Micronutrients				
	P_2O_5	K_2O	CaO +MgO		ZnO	CuO	Fe_2O_3	MnO	B_2O_3
CRG1	65	17	10	3	-	-	-	-	5
CRG2	60	22	10	2	0.5	2	3	0.5	-
CRG3	45	25	25	3	1	-	-	1	-

For the analysis of structure, this glasses were considered as a binary one: $z\mathrm{Me}_{2/x}\mathrm{O}\cdot(1\text{-}z)\mathrm{NFO}$ where Me are ion modifiers (K, Ca, Mg, Zn, Cu, Fe, Mn), z is a molar fraction of oxides and x is the valence of the Me atoms; NF is network former ions (P, Si, B). For $0 \leq z \leq 0.5$ the glass is ultraphosphate and for $z>0.5$ the glass is polyphosphate (Brow, 2000). Based on the chemical analysis of the glasses (Table 1), it is concluded that the CRG1 and CRG2 belong to ultraphosphate glasses, while CRG3 belongs to the group of polyphosphate glasses. Figure 1 shows the chemical stability of all three glasses in an acidic environment at a temperature of 37 °C. From Figure 1, it can be seen that the concentration profiles are similar. The dissolution process is initially very intense (initial phase), while after 15 h it slows down significantly (transitional phase) and enters the stationary phase (final phase). CRG1 and CRG3 dissolve faster than CRG2 (Figure 2) because the composition of this glass contains divalent and trivalent cations that connect the phosphate network and make it more resistant. Divalent cations form chelate structures, which are more resistant to the action of acids. CRG1 dissolves and has a slightly higher dissolution rate than CRG3. Including B_2O_3 into phosphate glasses often improve their chemical durability because of the formation of P-O-B bonds, which exhibit higher resistance to hydrolysis than P-O-P bonds. This small difference in dissolution rate is probably because the iconicity of the P-O-Ca bond is lower than that of the B-O-Ca and B-O-K bonds and it is more flexible and less resistant to the action of H^+ ions (Lee et al, 2022).

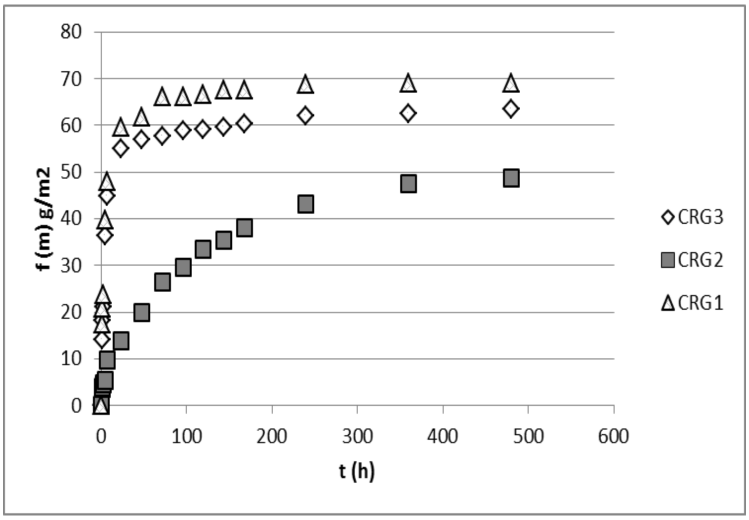

Figure 1. Dependence of normalized mass release f(m) on dissolution time at 37 °C

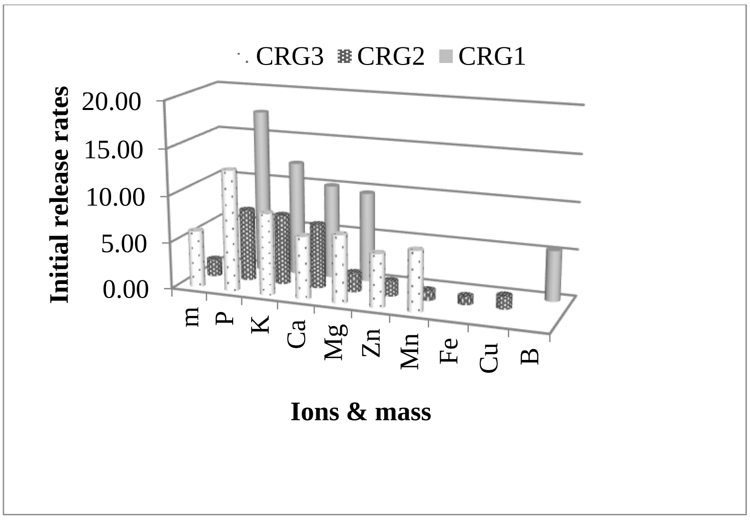

Figure 2. Initial release rates of the ions and mass

Figure 3 shows the influence of temperature on the dissolution process of CRG3. The concentration profiles for the other two glasses are similar (data not shown). It can be seen that with increasing temperature, the initial phase is shortened and the changes become abrupt (sharper). The final phase expands and the slopes of changes in this phase increase with temperature.

All three vitreous fertilizers were tested in real conditions for feeding different plants, in the greenhouse of the Faculty of Agriculture, University of Belgrade.

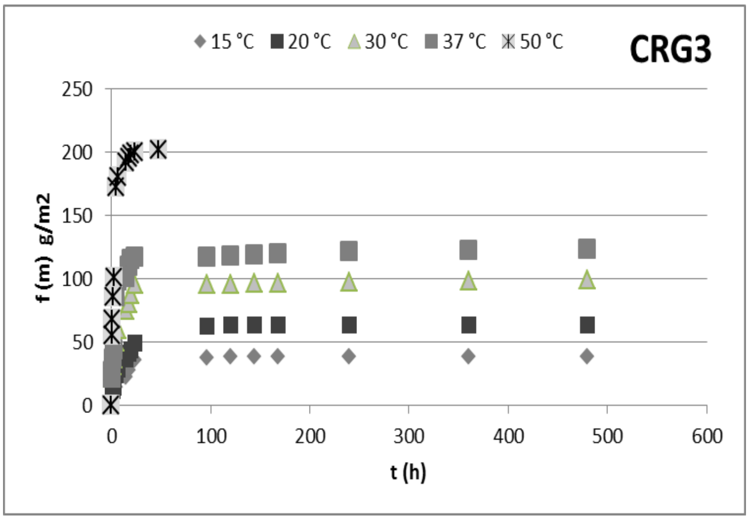

Figure 3. Dependence of normalized mass release f(m) on dissolution time for CRG3

The obtained results show that these fertilizers have a positive effect on the growth and development of plant crops. Table 2 shows some of the basic statistics indicators for examined quality parameters of Capsicum annuum L seedlings fed with CRG2.

Table 2. The basic statistics indicators for examined quality parameters of Capsicum annuum L seedlings

Parameters	Dosage of phosphate glass	I_v Interval of variation	$\bar{x} \mp s\bar{x}$ Arithmetical mean ∓ Standard error	M_e Median	C_v (%) Coefficient of variation
Plant height (cm)	0 (test)	25.1– 40.3	31.370 ∓ 1.638	30.450	16.508
	1 g/l	334 – 41.4	37.350 ∓ 0.890	37.000	7.535
	2 g/l	25.6 – 37.9	32.690 ∓ 1.297	33.700	12.545
	3 g/l	28.4 – 40.7	34.370 ∓ 1.279	34.150	11.764
	4 g/l	23.8 – 35.4	30.700 ∓ 1.271	31.650	13.090
Number of leaves	0 (test)	17.0 – 55.0	28.4 ∓ 3.407	26.000	37.931
	1 g/l	24.0 – 33.0	27.3 ∓ 0.803	26.500	9.307
	2 g/l	21.0 – 31.0	25.4 ∓ 1.861	24.500	13.789
	3 g/l	15.0 – 33.0	22.8 ∓ 0.876	21.500	25.807
	4 g/l	13.0 – 36.0	26.2 ∓ 2.973	30.500	35.886

Based on the parameters of development examined it was determined that the glass dosage of 1 g/l is optimal. This dosage was affected significantly by an increase in average height and the overground mass of the plants. Concerning other additives for improvement of the substrates (mineral fertilizers, vermicompost, etc.), by addition of polyphosphate glass, better development of pepper seedlings was attained.

Conclusion

This paper presents three phosphate glassy fertilizers (CRG1, CRG2, and CRG3) of different chemical compositions, the method of obtaining them, their dissolution rates in a medium that simulates soil conditions, and the effect of temperature on dissolution rates. The dissolution process is initially very intense (initial phase), while after 15 h it slows down significantly (transitional phase) and enters the stationary phase (final phase). CRG1 and CRG3 dissolve faster than CRG2 because the composition of this glass contains divalent and trivalent cations that connect the phosphate network and make it more resistant. With increasing temperature, the initial phase is shortened and the changes become abrupt. The obtained results show that these fertilizers have a positive effect on the growth and development of plant crops. Based on the parameters of development examined it was determined that the CRG2 dosage of 1 g/l is optimal for pepper seedlings (Capsicum annuum L).

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