S U M M A R Y

PRODUCTION OF PLANT BIOSTIMULANTS BASED ON POROUS CERAMICS

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To ensure safe and stable harvests, one of the most promising and environmentally friendly approaches is the use of plant biostimulants. According to Regulation (EU) 2019/1009 of the European Parliament and of the European Council, plant biostimulants are defined as "a product that stimulates plant nutritional processes independently of the product's nutrient content, with the sole purpose of improving one or more of the following characteristics of the plant or its rhizosphere: (a) the efficient use of nutrients; (b) tolerance to abiotic stress; (c) crop quality-related characteristics; (d) the availability of nutrients taken up from the soil or the rhizosphere."

Plant biostimulants, like certain fertilizers/soil conditioners, are also obtained from various by-products of the bioeconomy, such as used diatomaceous earth, a by-product from beer filtration, or bentonite, a by-product from wine filtration. The use of by-products reduces their environmental impact.

A new and highly efficient field is the development of porous ceramic products based on bioeconomy by-products, impregnated with nutrients that allow for their slow release, aimed at improving plant growth, soil fertility and the overall health of the ecosystem.

The porous structure of the ceramic granules ensures: optimal retention of air, water and nutrients in the root zone, reduction of soil compaction, improvement of drainage and enhancement of soil structure. This structure allows for the controlled release of nutrients for plants, ensuring their harmonious development.

This doctoral thesis aims to develop a technology for producing biostimulants based on porous ceramics, which are effective both in the optimal development of plants and in the nutrition of plants grown in the respective soils.

The aim of this study is to develop and optimize the technology for producing porous ceramic granules to fully utilize their potential by incorporating beneficial elements for plants (potassium, phosphorus, silicon) into the ceramics, in order to increase the loading of favorable biostimulant elements for them.

The objectives derived from this need to develop and optimize modern technology for producing porous ceramics with fertilizers and biostimulants are:

1) to produce porous ceramic products using local, unconventional raw materials: Bodoc clay, Valea Zălanului clay and Balint clay, diatomaceous earth from the deposits in Filia and Pătârlagele, along with by-products from the bioeconomy, such as silicon diatomite resulting from beer filtration (Sânsimion, Miercurea Ciuc) or bentonite from wine filtration (Miniș).

2) to optimize the technology for producing porous ceramics and impregnate them with nutrients beneficial for plant growth and development and to manufacture the quantities needed for conducting plant experiments;

3) physicochemical characterization of porous ceramics with impregnated nutrients;

4) testing the effects of porous ceramics on tomatoes, peppers and cucumbers;

The thesis is structured into two parts and contains 95 figures and 27 tables.

The first part represents the bibliographic study conducted on the addressed topic and is divided into three chapters.

Chapter I. Inorganic biostimulants for plants

The categories of biostimulants for plants are briefly presented, including the specific effects of plant biostimulants and inorganic biostimulants (particularly silicon and soluble silicon).

Chapter II. Porous ceramics as a support for controlled release of inorganic biostimulants/mineral nutrients.

The main uses of porous ceramic granules in agriculture are discussed, including: improving the characteristics of sandy soils; enhancing the characteristics of the growth substrate; effects on plant roots and the root microbiome; the influence of cation exchange characteristics on their use as soil conditioners; activation of processes that mobilize soil phosphorus reserves and the slow release of soluble silicon forms.

Chapter III. Production of porous ceramic granules and their physicochemical characterization.

This chapter covers the production of porous ceramic granules (methods of production; chemical transformations during the sintering process); the characteristics of porous ceramics (structure of porous ceramics, capillary action; water-binding capacity) and the functions of porous ceramics (functional groups for binding inorganic biostimulants).

The second part contains the original results of the thesis and is divided into three chapters.

Chapter IV. Ceramic granules that retain water and mineral nutrients (potassium) in the soil.

This chapter presents the materials and methods (raw materials – diatomite and Bodoc clay – for producing porous ceramic granules; production of porous ceramics; loading the granules with mineral nutrients); characterization of porous ceramic granules (physicochemical characteristics; structural and morphological characteristics of the porous ceramic granules); investigation of potassium desorption in aqueous solution; study of K+ migration through fertile soils; field experiment method (biological material and other types of materials); the influence of using porous ceramic granules – SAB/diatomite sludge and Bodoc clay – on the development of plants and tomato production in the field; physiological analyses of field-grown tomato plants and results and discussions (results on water and mineral nutrient retention and the structural and morphological characteristics of ceramic products); results regarding the influence of SAB granules on plant development and fruit production (determination of photosynthesis efficiency and stomatal resistance).

Based on the obtained results, the following key conclusions can be drawn:

- Porous ceramic granules are among the most effective products used in soil remediation and can be obtained through specific technological processes in the technical ceramics industry.
- The structure of a porous ceramic consists of particles separated by voids—called pores. These characteristics enhance and improve the aeration in the root zone as well as the capacity for storing water and air.
- Advantages of porous ceramic granules: they ensure moisture and air circulation, provide an aerated environment and retain water. Due to their high porosity and high absorption capacity, they can store a larger amount of nutrients, which helps maintain them in the root zone for a longer period.
- The purpose of using these granules is the gradual release of mineral nutrients at a rate that ensures their absorption by plants. They have significant effects on improving soil drainage and eventually disintegrate within a relatively short period.
- The porous ceramic granules were analyzed physically according to existing standardized methods: apparent density, apparent porosity and adsorption capacity. The morphology of the surfaces of the obtained samples was examined using SEM microscopy.
- Based on the physicochemical analyses performed, it was found that among the porous ceramic granules produced, the most effective was S.A.B.5 with 80% diatomaceous earth and 20% Bodoc clay.

- The advantage of the biostimulant porous ceramic granules – S.A.B.5 – is that they are composed of eco-friendly raw materials (pore-forming) – diatomaceous earth-silica from beer filtration and Bodoc clay – which do not contaminate the soil, groundwater or plants. After decomposing over time, they leave no residual traces. Their characteristics are: color: brownish-red; apparent density: 0.67 kg/dm^3; apparent porosity: 33.67%; and adsorption capacity: 88.23%.
- From the study of K+ migration through aqueous solution, it was concluded that thermal treatments do not significantly affect the release of potassium from the porous ceramic granules.
- Additionally, the study of K+ migration through fertile soil revealed that the release of K+ through fertile soil is slower compared to its release in aqueous solution.
- Considering the characteristics of the S.A.B.5 granules, their use is recommended for practicing sustainable agriculture.
- Field studies have demonstrated that ensuring optimal availability of potassium during cultivation, along with water retention and soil aeration around the roots, leads to even better plant growth results.

Chapter V. Ceramic granules that retain water and mobilize phosphorus reserves

The materials and experimental methods are developed (raw materials: bentonites and Bodoc clay; obtaining porous ceramics; loading the granules with mineral nutrients; characterization of the ceramic granules - physical-mechanical characterization and structural and morphological characterizations; the method of doing the experiment in the greenhouse) ; the influence of the use of porous ceramic granules-BA/Bentonite from wine filtration and Bodoc clay on the development and production of tomato and pepper plants grown in the greenhouse; results and discussion (results regarding the obtained porous ceramic granules that retain water and phosphorus in the greenhouse and the physicochemical characteristics – TGA, BET, XRD, FTIR, SEM).

Additionally, the results regarding the influence of the granules on the fruit production of tomatoes grown in the greenhouse in 2021 are presented, as well as the experimental results on the effect of porous ceramic granules on the physiology and quality of the production of tomatoes and peppers cultivated in the greenhouse in 2021 (determination of stomatal resistance).

In conclusion, it can be stated that:

- The use of clay granules with bentonite by-products increases the drought resistance of peppers subjected to testing. Additional treatment with KNO3 provides an extra level of drought resistance, while the addition of monoammonium phosphate (NH4H2PO4) does not alter the effect of the clay granules with bentonite by-products. A higher concentration of phosphate ions

(V7) nearly completely inhibits the drought resistance of the tested plants. Kivelli tomatoes responded best to the V4 and V7 variants.

- Pink Impresion tomatoes responded best to the following treatments: V3, V2, V4 and V7.
- The Claudius peppers responded best to the treatments: V4, V5, V3 and V6.

Treatments V2-V7 refer to:

- V2: Plants treated only with PCG50 with high capillarity;
- V3: Plants treated only with PCG60 with high capillarity;
- V4: Plants treated with PCG50 containing K;
- V5: Plants treated with PCG60 containing K;
- V6: Plants treated with PCG50 containing PO_4^{3-};
- V7: Plants treated with PCG60 containing PO_4^{3-}.

Chapter VI. Porous ceramics with controlled silicon release

The materials and methods are presented (biological materials, methods and organization of experiments; development of products based on porous ceramics with controlled silicon release; characterization of porous ceramics with controlled silicon release; testing of porous ceramics on Momordica charantia; determination of the influence of treatments with silicon-releasing porous ceramics on the accumulation of bioactive compounds in bitter melon fruits, on physiology and on production levels); results and discussion (production and characterization of porous ceramic granules; influence of treatments with silicon-releasing porous ceramics on the production and physiology of M. charantia plants; characterization of the accumulation of bioactive compounds in M. charantia plants).

In conclusion, it can be stated that:

- Porous ceramic granules were developed where not only a simple passage of nutrient fluid through the pores occurs, but a complex sorption–desorption phenomenon takes place within the soil–granule–plant system.
- Among the properties of porous ceramics, the following were highlighted: apparent density, adsorption capacity, apparent porosity, pore distribution and size, phase composition and structure, as well as mechanical resistance.
- It was found that porous ceramic formulations containing diatomite have a high capacity for silicon release and result in beneficial effects on bitter melon plants, including optimization of photosynthesis processes, increased production levels and accumulation of bioactive compounds.

Chapter VII. General conclusions and perspectives

Due to their good physicochemical properties, porous ceramics stimulate the growth of the plant root system, improve resistance to water stress, as well as resistance to trampling and detachment.

Porous ceramics are an accessible product for obtaining growth substrates, which are important not only for maintaining green spaces in parks but also for producing vegetable and flower seedlings or for growing vegetables in protected environments.

Porous ceramic masses have been synthesized using local clays—Bodoc, Balint, refractory clay—as well as diatomite from Pătârlage and Filia and additives from bioeconomy by-products: diatomite sludges from beer filtration (Sânsimion and Miercurea Ciuc) and bentonite sludges from white and red wine processing (Miniș).

The technology used is that employed in the ceramics industry, with the main phase being shaping, specifically granulation through rolling. Any form of compaction was avoided to achieve a product with appropriate porosity.

The porous ceramic granules were investigated through physical characteristics (absorption, density, porosity), SEM images, IR, etc. The thermal processes during the sintering of ceramic products were controlled through TGA analyses.

The size and distribution of pores significantly affect the strength and durability of ceramics. Typically, high porosity ensures greater water absorption and simultaneously increases the capacity to absorb biostimulant nutrients in the product. The higher the porosity and water absorption value, the more biostimulant nutrients the ceramic product can absorb, which benefits plant growth and development.

Biological tests with porous ceramic granules have demonstrated the presence of specific biostimulant effects for plants.

It is worth emphasizing the positive effect of the SAB5 product with KNO3 nutrient and the BA50/ Bentonite from wine filtration (50%) and Bodoc clay (50%) and BA60/ Bentonite from wine filtration (60%) and Bodoc clay (40%), with KNO3 nutrients on the quality of tomatoes and peppers.

A significant positive effect of treatments with SAB5, BA50 and BA60 products on plant physiology, specifically the efficiency of water use determined by stomatal resistance, was observed for both tomato and pepper crops.

It should be emphasized that the SAB5 mixture contains 80% diatomaceous earth sludge from beer production, along with Bodoc clay. The BA50 and BA60 mixtures also contain a high proportion of bentonite sludge from wine production, 50% in BA50 and 60% in BA60. The use of these sludges presents economic advantages (saving on more expensive raw materials) and ecological benefits (environmental protection).

Based on the results obtained from the experiments, it is observed that BA50K/Bentonite from wine filtration 50% and Bodoc clay 50% with KNO3 content had a significant effect on the crops. Thus, it can be stated that "porous ceramic granules" are effective nutrients for "greenhouse plants."

The ceramic granules containing diatomite release soluble silicon gradually, which has beneficial effects on bitter melon plants.

The results obtained demonstrate that using porous ceramic materials, which include bioeconomic by-products and are impregnated with nutrients, allows for the production of safe and stable horticultural crop yields (tomatoes, peppers and bitter melons) with an increased content of bioactive compounds.