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POROUS CERAMIC GRANULES AS INORGANIC SOIL CONDITIONER

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Abstract

Porous ceramic granules (PCGs) present an interconnected pores architecture, which mimics the spatial arrangement of the pore spaces and of the solid particles, mineral and/or organic, in the soil. More than 2/3 of the volumes of the ceramic granules used as soil improvers are pores of different sizes – macro, micro and nanopores. Around one half of these pores are capillary pores, which retain and slowly release water and mineral nutrients. The other half of the pores are non-capillary pores, retaining gases and supporting soil aeration. This PCGs porous structure, related to the efficiency as soil improver, is highly compaction-resistant, making PCGs an effective soil conditioner for cultivated plants that support high traffic, such as turf and ornamental garden plants. This paper reviews the use of porous ceramic granules as inorganic soil improver for horticultural plants.

***Key words**: porous ceramic granules, capillary pores, water and nutrient release, soil aeration, compaction.*

INTRODUCTION

For decades, one of the main goals in both horticulture and agriculture has been to increase soil fertility, affected by agricultural practices. In particular, sandy soils require more attention, due to their poor water and mineral nutrients. This problem of soil fertility constant degradation is solved by the application of various organic and inorganic soil improvement material (Bigelow et al., 2004; Szegi, 2009). The sand content of the Earth's land reaches 7%. However, sandy soils in Romania occupy about 500,000 ha, of which 150,000 ha is semi-bound or quicksand (Dumitru et al., 2011; Josan et al., 2000). The use of soil improvers of both organic and inorganic origin creates favorable properties for soil fertility, especially for the physico-chemical properties and microbiological activity of sandy soils (Kocsis, 2018; Makádi, 2010). However, the organic soil conditioners are biodegradable over time and their beneficial effect is not a long lasting-one. The inorganic soil conditioners effects are for a longer period, due to their longer stability. The inorganic materials that can be used as soil conditioners include by-products of various origins, including those from bioeconomy, e.g., spent diatomaceous earth from mini-breweries. The production and utilization of soil conditioners close the loop in the (bio)economy value chains in a biomimetic manner (Makádi, 2010; Roșu et al., 2016). Such byproducts are regulated for their use as soil improvers and should contain a small quantities of contaminants - e.g., potential toxic metals, entero-toxigenic bacteria.

Most studies with soil improvers are related to their influence on soil structure and crop yield. Several studies were conducted also on the extent to which soil conditioners can affect the sorption capacity of colloid-poor soils (Bigelow et al., 2004; Kocsis, 2018).

A particular case of soil conditioners is related to restoring lands following major construction works, ornamental horticulture (new gardens) and golf course greens. In these situations, occur a total reconstruction of the soil. For example, to accommodate golf course greens, the soil layer is often removed from its location and replaced with sand-based media to prevent compaction and improve drainage. Several soil modifiers have been used for sand-based grassland media, such as calcined clay, diatomite, porous ceramic, expanded shale, perlite, pumice, sintered fly ash, slags, and vermiculite. Due to the low water and nutrient holding capacity of sand-based soils, several inorganic modifiers are proposed to eliminate defects in sandy soils, i.e., to increase water retention and to maintain high drainage and aeration properties, and to improve Cation Exchange Capacity - CEC (Guertal & Waltz, 2008; Jing, 2013; Li, 2001; Szegi, 2009)

The development of porous ceramics began in the 1970s, but more recently, due to their industrial, agricultural, and horticultural applications, they have become increasingly important. The pore size formed in the ceramic material is greatly influenced by the starting raw materials and the production method. The porosity value of porous ceramics is variable, between 20 and 95%. After sintering, the porous ceramic material consists of three phases: a ceramic solid phase, a water phase, and an air (gaseous) phase that fills the pores (Al-Naib, 2018; Liu & Chen, 2014; Roșu et al., 2016).

Inorganic porous ceramics promote water retention in sandy soils, have beneficial effect on soil structure, stimulate the uptake and utilization of mineral nutrients. Such soil conditioners could be included in soil or could be applied at the surface of the soils (Guertal & Waltz, 2008; Kocsis, 2018; Stefanovits et al., 1999).

This study aims to review the main features of the porous ceramic granules related to their use as (sandy) soil conditioners and the improvement of the soil physico-chemical and biological characteristics resulted after their application.

MATERIALS AND METHODS

The materials used are represented by scientific publications from around the world.

This paper reviews the use of porous ceramic granules as inorganic soil improver for horticultural plants.

RESULTS AND DISCUSSIONS

POROSITY FEATURES OF THE CERAMIC SOIL IMPROVERS

An essential feature for the ability of a ceramic granule to act as a soil conditioner is porosity (Figure 1). Porous ceramic granules mimic the structure of the soils, presenting three distinct phases: a solid phase, comprising the ceramic support, a water/liquid phase, consisting of water retained by the hydrophilic surface of ceramic pores and a gaseous phase, filling the empty part of the ceramic pores (Roșu et al., 2016). Essential for soil water retention and CEC improvement are both porosity and pore surface hydrophilicity.

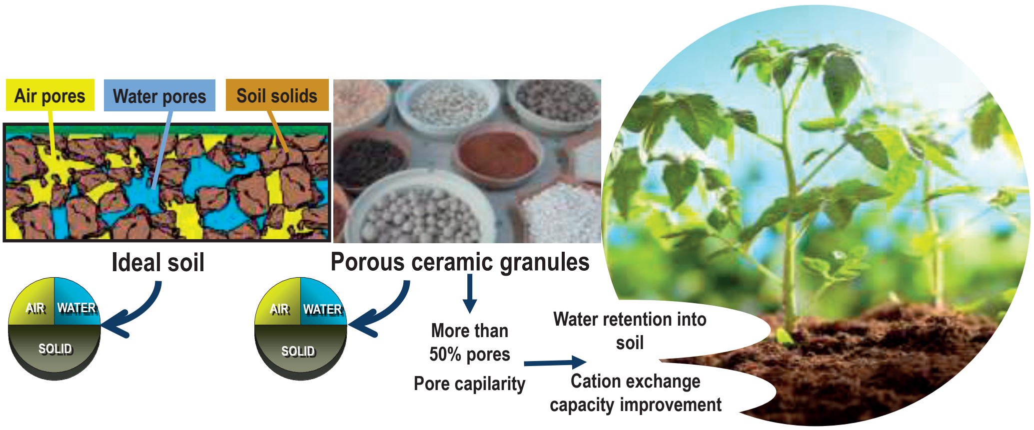
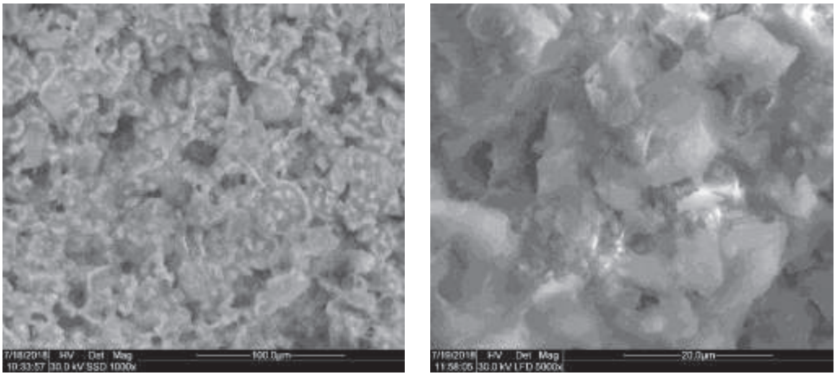


Figure 1. The essential features related to ability of a ceramic granule to act as soil conditioner - porosity and hydrophilicity of the pores surface

Ceramics are rigid materials due to the covalent bonds that hold them together. Their pore systems greatly depend on the size of the particles and type of shaping. However, to increase the porosity of ceramics, wood flour, sawdust or polystyrene beads are mixed even during production, which, after heat treatment, create pores - sacrificeal scaffolds (Horváth, 2019). According to their structure, differences are distinguished between open-pore ceramics in which most cells are in contact with each other (Figure 2), and closed-pore ceramics, where the pores are independent from each other, without communicating channels. However, there are also mixed structures, when both open and closed structures occur within a granule (Fazakas, 2006; Horváth, 2019).



a b

Figure 2. Open-pore ceramic SAB25 in which pores are communicating with each other and ensure fluids transport. SEM images of the cross-section (a) 1000x and (b) 5000x of SAB25-PCG (original images)

Pore type and manufacturing methods

Porous ceramics are classified as high porosity ceramics, of 20 to 95% pores. If the porosity of any ceramic body is determined, a distinction is made between open porosity (externally accessible) and closed porosity. The sum of open and closed porosity is understood to mean total porosity. The (nano) porous size of porous ceramics can be divided into 3 types depending on the pore diameter: microporous (less than 2 nm), mesoporous (between 2-50 nm) and macroporous (> 50 nm) (Al-Naib, 2018; Dittmann et al., 2013). The ideal nanoporous structure of the porous ceramic used as soils conditioners should be similar to that of allophane, a nanoporous clay specific to Andosols - volcanic soil from Andes. Allophane has a large pore volume, and a fractal 3 porous fractal arrangement, resembling to a labyrinth (Woignier et al., 2015). Such 3D nanostructures are also present in the siliceous natural nanomaterials (SNNMs) used as soil improvers, i.e., natural zeolites and diatomaceous earth (Constantinescu-Aruxandei et al., 2020).

The division of the pore space can be distinguished by the size of the pores and the pores characterized by different pore diameter limits, according to the forces acting on the fluid flowing in the pore space. Within the pore space, from a practical viewpoint, two types of pores can be distinguished: (i) the group of capillary/micro/matrix pores; (ii) the group of non-capillary/macro/structural pores (Hernádi et al., 2017).

In terms of water movement, macropores are rapidly-drainable-pores (RDPs). The micro-pores are composed of capillary pores with two different pore diameter ranges, which correspond to slow-draining and water-retaining pores, respectively slowly drainable pores - SDP; water holding pores - WHP) (Hernádi et al., 2017).

For the preparation of porous material, beside the sacrificial scaffold techniques, already mentioned, other methods such as layer by layer deposition, pressing, pelletizing and the capillary suspensions are used (Table 1). (Chen et al., 2019; Dabare & Svinka, 2014; Dittmann et al., 2013; Liang et al., 2007; Saponjic et al., 2015; Surabhi, 2012; Yoo et al., 2008).

Table 1. Pore characteristic according to manufacturing method

Manufacturing method	Water absorbtion	Apparent density	Porosity	CEC	Capillarity	Reference
Sacrificeal scaffold	++	+	++	+	+	(Surabhi, 2012)
Layer by layer deposition	+	+	+	+	+	(Liang et al., 2007)
Pressing	+	+	+	+	+	(Saponjic et al., 2015)
Pelletizing	+++	+++	+++	+++	++	(Dabare & Svinka, 2014; Yoo et al., 2008)
Capillary suspensions	++	++	+++	+	++++	(Dittmann et al., 2013)

+: quite good; ++: good; and +++: very good/excellent

During production of a porous ceramic body, the formation of porosity is significantly influenced not only by the manufacturing techniques, but also by the raw materials and binders used and their distribution and, last but not least, by the sintering process, which also affects the final porosity, pore connectivity (Al-Naib, 2018; Surabhi, 2012).

Dittmann et al. (2013) introduced a method by which macroporous ceramics can be produced by capillary suspensions. By their method, 60% higher porosity can be achieved. To adjust porosity and pore size, the Al_2O_3 model system was used (Dittmann et al., 2013; Weiss et al., 2019). In another production method, after grinding and wetting the clay, the granules are burned in a tube furnace rotating at 1150°C. The moisture content of clay becomes vapor under the action of heat, inflating the granules and making them porous. Due to this porosity generated by water vapors, the application of burned clay to the soil gives to the plants' rapidly developing roots extra aeration. The clay granules produced by this method can be used alone (e.g. in hydroponic plant cultivation) or mixed with other materials as a growing substrate (Guertal & Waltz, 2008; Profile, 2021).

Pore analysis and characterization

The number of pores and their distribution are analysed and characterized by several methods, including X-ray diffraction, scanning electron microscopy, penetration porosimetry (Szegi, 2009).

X-ray diffraction characterizes the phase composition of the raw materials and the sintered products. The microstructural morphology (external and sequential structure of the granules) is observed by scanning electron microscopy (SEM). The porosity could also be estimated from the bulk density of porous ceramic materials, using the Archimedes technique (Al-Qadhi et al., 2019; Anovitz & Cole, 2015; Dabare & Svinka, 2014; Dutra et al., 2019; Jing, 2013). Pore size distributions are usually determined by mercury penetration porosimetry but can also be measured by optical and electronic examination of polished cross-sections and X-ray computed tomography (Al-Naib, 2018; Al-Qadhi et al., 2019) Water-based porosimetry is useful for determination of the macropores volumes (Andersson et al., 2013).

Capillary action and water movement

Soil, water and gas exchange is affected by several factors such as: pore volume, pore size, distribution in the soil. The vertical and lateral drainage of water in the soil is large through gravitational forces, so it occurs through non-capillary soil pores. In contrast, the upward movement and redistribution of water takes place through the capillary-pores (Amer et al., 2009; Stefanovits et al., 1999).

Under the influence of adhesive and capillary forces, the interaction between the solid phase and water is realized. This explains why some of the soil moisture adheres to the surface of the particles, while the other part is located in the pore space itself. In order for this adhesion to occur between water molecules and soil particles, the dipole nature of the water molecules and electrical charging of the finer soil particles is required (Hartman, 2008; Stefanovits et al., 1999).

Water entering the capillaries cannot be retained by larger pores as it is rapidly discharged by gravity. The water-retaining and water-lifting ability in capillaries can be attributed not only to adhesion forces between water and soil particles, but also and cohesion forces between water molecules. Capillary moisture also dissolves large quantities of plant nutrients and other compounds, which are transported by soil water to higher suction areas (Hargitai, 1985; Stefanovits et al., 1999).

Depending on the water moving in the soil, the filling of the capillaries can occur from the water leaking downwards (dependent capillary moisture) or from the groundwater (supporting capillary moisture). In the case where the capillaries are charged from top to bottom, it is a slower process, and the capillaries fill up from the infiltrating rainwater or irrigation water so that these capillaries are not in contact with groundwater. In capillaries feeding below, i.e. from groundwater, the capillary moisture decreasing from groundwater is constantly replenished by evaporation (Hartman, 2008; Stefanovits et al., 1999).

CATION EXCHANGE CHARACTERISTICS

Ion exchange processes play an important role in soil, the importance of which has been discovered in soil-related research. Ion exchangers are solids that contain ionic groups that are positively or negatively charged, yet can exchange their free-moving ions with other but equally charged counterions (Simándi, 2011).

The ion exchange capacity is mostly related to layered lattice aluminosilicates as well as clay minerals. Clay minerals with a trivalent cation in the octahedron and tetravalent silicon in the tetrahedron have a significant cation exchange capacity, as well as smectite (montmorillonite) type silicates (Nagy, 2017).

For efficient nutrient replenishment, it is essential to know the cation exchange capacity. The CEC test provides an answer to how much cation the tested soil can retain. The higher the CEC, the more cations can be bound. The clay and organic matter particles that make up the soil have a negative charge. In doing so, they attract positively charged particles, but repel negatively charged ones. The essence of the cation exchange capacity is that cations adhering to negatively charged material and organic matter particles can be replaced by other cations, i.e., exchangeable. For example, potassium can be replaced by calcium or hydrogen or vice versa (Mengel, 2014; Stefanovits et al., 1999). In the soil solution, in most cases, only 6 cations are present in larger amounts, so these compensate for the negative charges of the colloid. Thus, these cations, which equalize the negative charges of the colloid, are divided into two groups:

✓ Exchangeable acidifying cations: H_3O^+ and Al^{3+}.

✓ Exchangeable strong base cations: Ca^{2+}, Mg^{2+}, Na^+, K^+ (Szalai & Jakab, 2012).

MAIN APPLICATION OF POROUS CERAMIC SOIL IMPROVERS

Nowadays, agricultural and horticultural soils are constrained by several inherent defects, most of them of anthropogenic origin. Various soil improvers serve to eliminate the defects of these soils and to make the soils more fertile (Füleky et al., 2011). The use of porous ceramic granules (PCGs) to improve soil quality and crop yield is an emerging technology. PCGs are primarily used to improve degraded soils and constructed lands, as their porous structure is generating a high specific surface area. Due the large pores volumes and CEC area, PCGs improve soil water retention, plant nutrient uptake and soil aeration, as well as preventing nutrient leaching from the soil (Table 2) (Guertal & Waltz, 2008; Kocsis, 2018; Profile, 2021)

Table 2. Advantages and disadvantages of porous ceramic-based soil conditioners

Advantages	Disadvantages
Improves physical soil structure (Guertal & Waltz, 2008) Improves sand-based root zones (Li, 2001) Resist to compaction (Profile, 2021) Water retention (Bigelow et al., 2004) Facilitate healthy root systems (Profile, 2021)	Considerable production cost (Liu & Chen, 2014)

A wide range of these PCG soil improvers is now commercially available to modify and improve the physical and chemical properties of sand-based greens, tees, yards, beds, containers, and sports fields. The effectiveness of soil improvers depends to a large extent on the existing properties of the soil to be modified and the amount added (Profile, 2021; Szegi, 2009).

Improvement of the sandy soil characteristics

The disadvantage of sandy soils is that a large porous system can form between large elementary particles, thus they cannot drain or store water and therefore dry out quickly. This disadvantage is also related to the low content of colloidal components that would allow water and nutrients to be trapped, avoiding leaching into the deeper layers and contamination of the groundwater. Some sandy soils are also prone to compaction (Füleky et al., 2011; Miguel & Vilar, 2009; Szegi, 2009),

To improve the unfavorable physico-chemical properties of sandy soils, several agrotechnical methods or various technologies suitable for soil improvement were used (Füleky et al., 2011; Szegi, 2009) Briefly, the properties of sandy soils can be improved by:

✓ physical soil improvement methods: fertilization, inorganic soil conditioners - clay granules, porous ceramic granules (Andreola et al., 2021);

✓ chemical soil improvement methods: with artificial additives, such as superabsorbent anionic polymers (Eneji et al., 2013; Lejcuś et al., 2018; Panova et al., 2021);

✓ biological soil improvement methods: stable fertilization or the use of a material that is rich in colloids, as this layer has to be spread at a depth of 60 cm, as a result of which the nutrient and water management of the soil is also improved (Füleky et al., 2011).

Studies suggest that the inorganic soil conditioners are the most effective in improving sandy soil properties. For example, it was shown that calcined porous ceramics mixed with sand perform better than peat and chemical soil conditioner in improving water and nutrient retention and increasing oxygen levels in the root zone, while maintaining sandy soil drainage. These ceramic porous particles also retain water and release it to the plant as needed, delaying the need for irrigation (Profile, 2021).

By examined the effect of different compositions and amounts of inorganic soil conditioners, was reported that bermudagrass grown in sandy soil, modified with zeolite, calcined clay, diatomaceous earth or clay binder, diatomaceous earth, have up to 16% more available water, comparing the untreated control.

Improvement of the growing substrate characteristics

Growing substrate are used to cultivate plant in protected environment (e.g., greenhouses or nursery) or in constructed land - e.g., sand based turf media. Many types of calcined and expanded clays, diatomaceous earth, zeolites or other kiln-fired porous ceramic materials were used to improve the characteristics of the growing substrate used in greenhouses and nursery (Andreola et al., 2021; Gül et al., 2005; Ronga et al., 2020). The porous ceramic granules are particularly suitable for urban agriculture and vertical farming, due to their lightweight characteristics (Andreola et al., 2021). Simultaneously, in the industry of constructed greens(lands), the use of inorganic modifiers to replace peat has also become common (Li et al., 2000).

Numerous studies have been conducted on the efficacy of inorganic modifiers, with mixed results (Hargitai, 1985; Kappel, 2006; Sarkar & Kim, 2015). Inorganic soil modifiers are proposed when using grasslands to alleviate soil compaction, increase water retention and hydraulic conductivity, and improve many other physical properties of the soil (Bigelow et al., 2001).

Li et al. (2000) gave inorganic modifiers in sand-based golf ground - porous ceramic clay (PCC), calcined diatomaceous earth (CDE) and polymer coated clay - with the aim of determining their physical properties in sand-based media and determining the effects of these modifiers. According to their research, it was found that those treated with PCC had 7-8% higher cation exchange capacity (CEC) and also improved compaction compared to controls. Water retention also improved with the use of CDE. However, their research in the laboratory simulated changes during the winter, i.e., how the freeze-thaw cycle affects volume density, and concluded that PCC increased by 2.2%, CDE by 2.5%, and control. It reduced the bulk density by 7.2% (Li et al., 2000).

Porous ceramic granules (PPC) help to permanently improve root zones, increase oxygen levels, and retain water and nutrients. PPC soil improvers replace peat and other inferior products in native soil and sand mixtures. The secret of PPC granules is that a ceramic particle decomposes only 3% in 20 years, providing decades of ideal conditions in the root zones of golf greens, fairways, landscaping beds. They make it easier to work the soil, help the plant grow faster, reduce the frequency of watering, make the use of fertilizer more efficient, thus producing healthier lawns and ornamentals (Profile, 2021).

The inorganic porous ceramic particle has a pore space of 74%, of which 39% contains capillary (water) and 35% non-capillary (air) pores. Thanks to the high pore space of the material, it helps to resist compaction and treats moisture/drainage. Ceramic particles are incorporated into the root zones of the soil or used as cover layers (Profile, 2021).

In addition, inorganic soil conditioners have been developed that wrap nutrients in clay-based porous ceramic montmorillonite particles, protecting the plant from nutrient loss. These organically managed soil products improve the soil biology of the plant, helping to preserve the flow of water and oxygen in the roots of the plants in the easily compacted soil. It can be applied to sports grass as well as agricultural fields (Spittle, 2014).

EFFECTS ON PLANT ROOTS AND SOIL MICROBIOTA

Inorganic soil improvers, applied in granular form (porous ceramic, clay granules, perlite, lava powder), in addition to their long-lasting effect on soil characteristics, have also beneficial effect on the roots of plants. Inorganic soil improvers increase the oxygen level in the root zone, improve water and nutrient management, prevent the soil and roots from drying-out quickly and control overflowing. Due to their porous structure, porous ceramic granules provide a uniform nutrient concentration, creating a good habitat for plant roots (Bigelow et al., 2004; Guertal & Waltz, 2008; Nagy, 2017).

The application of organic and inorganic soil improvers/conditioners to the soil/plant growing medium not only increases the availability of plant nutrients. The soil improvers influence also both long- and short-term land use changes in the composition and activity of the soil microbial community (Ikoyi et al., 2020; Kocsis, 2018; Liu et al., 2017). Beneficial soil microorganisms are essential for plant development. In nutrient poor soils, introduction of small quantities of mineral nutrients leads to a rapid proliferation of soil microbes, which could turn to competitors for the plants nutrient usage. Large quantitate of mineral fertilizer promote soil acidification and favours the growth of fungi, including plant pathogenic fungi (Makádi, 2010). Due to their capacity to bind nutrients inorganic soil improvers buffer mineral nutrients variations and reduce the negative influence of fertilizers variations on soil microbiota (Fomina & Skorochod, 2020).

Recently, it was demonstrated that large macropores present in soil promote development of soil microorganisms (Harvey et al., 2020; Sun et al., 2020). This is mainly due formation of microhabitat which are driving trophic interactions, allowing beneficial bacteria and fungi to escape from meso- and macrofauna predators (Erktan et al., 2020). Porous ceramics offer shelter to the beneficial microorganisms, which proliferate inside the macropores and develop biofilms on the surface of the granules (Nikolajeva et al., 2012). The use of the porous ceramic granules as carrier for plant biostimulant *Trichoderma* was patented (Raut et al., 2017).

Weathering of porous clay granules and formation of the soluble silicon species was demonstrated (Vu et al., 2011). In the case of porous ceramic/calcined clay soil improvers this effect resulted from their interaction with soil microbiota could explain several effects (as crop quality improvement or increase tolerance to stress) which are rather specific for plant biostimulants (Constantinescu-Aruxandei et al., 2020). By definition, plant biostimulants enhance/benefit nutrient uptake, increase plant tolerance to abiotic stress and improve quality of the crop yield (Du Jardin, 2015). Soil improvers also enhance benefits nutrient uptake, due to their influence on soil CEC.

Improvement of the yield quality and/or increase tolerance to abiotic stress, demonstrated for several silicates-based soil improvers are most probably related to their interaction with soil microorganisms and slow released of the soluble silicon species (Constantinescu-Aruxandei et al., 2020).

CONCLUSIONS

One of the challenges today is to provide fertile, stable soil for our plants and soil microbiome. To solve this challenge, numerous inorganic soil improvers (pumice, grounded lava stone, expanded clay, porous ceramics, zeolites, diatomaceuous earth) are used. These inorganic soil improvers influence the chemical and biological properties of the soils, especially of sandy soils, and of growing substrate (Guertal & Waltz, 2008; Kappel, 2006; Li et al., 2000).

In the case of the porous ceramic granules, the cost reduction for their production involve use of the less expensive raw materials, including bioeconomy byproducts. Porous ceramic granules are suitable for the reclamation of the (sandy) soils because their structure is similar to the ideal soil (Guertal & Waltz, 2008; Kappel, 2006; Li, 2001; Roșu et al., 2016).

Improving the water holding and water holding capacity of sandy soils is a major challenge (Bigelow et al., 2001). The results of several years of research and applications have shown that the use of porous ceramic granules as soil improvers can increase soil stability, improve the physicochemical and biological properties of the soil, and improve the water management and aeration of the soil, mainly due to the capillary and non-capillary pores. Their usage in lawn and golf courses prevent compaction, resistance to stepping and detachment (Roșu et al., 2016). Porous ceramic granules offer sheltering micro-habitats for soil microorganisms, stimulate root formation, promote plant growth and development (Li, 2001; Li et al., 2000; Liu & Chen, 2014; Profile, 2021).

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