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BIOLOGICAL NUTRITIONAL VALUE OF ZEOLITE-BASED SOIL ENHANCERS

BIOLOŠKA HRANLJIVA VREDNOST OPLEMENJIVAČA ZEMLJIŠTA NA BAZI ZEOLITA

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ABSTRACT

A series of greenhouse experiments were conducted in order to determine the biological nutritional value of the substrate mixtures based on newly designed zeolite soil enhancers made to replace an earlier registered commercial enhancer (ZeoPlant™). Lettuce (*Lactuca sativa* L.) was used as a test species. Plant height, number of leaves, and fresh plant mass were measured. During the preliminary experiments, the optimal ratio of enriched zeolites in the peat-based substrate mixtures was verified (about 25% volumetric), as well as the usability of Pirotski peat for the preparation of substrate mixtures. Enriched zeolites (EZa, EZb, EZc, EZd) were mixed in optimal ratio with Pirotski peat and compared to *a* commercial zeolite-based substrate mixture that was used as a control treatment. The control treatment showed the best results. On the other side, the differences between other treatments were not significant, but they indicate that some of the examined soil enhancers have a great potential for application in vegetable seedling production.

Keywords: *substrates, zeolites, natural peat, vegetable, seedlings.*

REZIME

U objektima zaštićenog prostora Instituta za povrtarstvo u Smederevskoj Palanci, obavljen je niz eksperimenata s ciljem utvrđivanja biološke hranljive vrednosti novostvorenih oplemenjivača zemljišta na bazi zeolita osmišljenih da zamene ranije registrovani komercijalni oplemenjivač (ZeoPlant™) koji je u ogledima korišćen kao kontrolni tretman. Praćeni su visina biljke, broj listova i sveža biomasa zelene salate (*Lactuca sativa* L. var. *Neva*) koja je korišćena kao test biljka. Tokom preliminarnih eksperimenata verifikovan je optimalan odnos obogaćenih zeolita u mešavinama supstrata na bazi treseta (oko 25% zapreminski), kao i upotrebljivost pirotskog treseta za pripremu mešavina supstrata za proizvodnju rasada povrća. U toku finalnih eksperimentalnih aktivnosti, prirodni zeoliti oplemenjeni su različitim tehnološkim postupcima, organskim i mineralnim đubrivima (varijante EZa, EZb, EZc i EZd) i zatim korišćeni za prirpemanje supstrata za proizvodnju rasada zelene salate. Oplemenjeni zeoliti mešani su u optimalnom odnosu sa pirotskim tresetom čineći tretmane (A, B, C i D) a njihova hranljiva biološka vrednost upoređena je sa hranljivom biološkom vrednošću supstratne smeše pomenutog treseta sa optimalnim udelom komercijalnog zeolita (kontrolni tretman). Na osnovu prikupljenih podataka utvrđeno je da je kontrolni tretman pokazao najbolje rezultate za sve ispitivane osobine. S druge strane, razlike između ostalih tretmana nisu bile statistički značajne, ali ukazuju na to da neki od ispitivanih oplemenjivača zemljišta imaju značajan potencijal za primenu u proizvodnji rasada povrća i mogu biti adekvatna zamena ranije registrovanog komercijalnog oplemenjivača zemljišta na bazi zeolita. Za te svrhe, prirodne zeolite odgovarajuće granulacije trebalo bi obogatiti većim dozama tj. koncentracijama hraniva, posredstvom organskih i mineralnih đubriva.

Ključne reči: *supstrat, zeoliti, treset, povrće, rasad.*

INTRODUCTION

High-quality seedlings are the main objective of every nursery involved in vegetable production. To achieve this goal, besides greenhouses, different pots and containers, vigorous seeds and other necessary items, producers need appropriate substrates. Growing substrates must fulfill some of the demands such as good porosity, water retention and demands related to air and water proportion, high nutrient content and nutrient availability, low electroconductivity (EC), optimal pH value, which is different for each species grown. They should be pest-free, cost-effective, available on the market, etc. Following the above-mentioned, for substrate preparation, different materials such as various types of natural peat, composts prepared using green waste, municipal solid waste compost, manure, pine barks, olive mill residues, grape marcs, used mushrooms substrate, and other materials could be used (*Ilin et al., 2002; Ilin et al., 2003; Gutierrez-Miceli et al., 2007; Ribeiro et al., 2007; Zmora-Nahum et al., 2007; Herrera et al., 2008; Carmona et al., 2012; Zhang et al., 2012; Ben Jenana et al., 2013; Morales-Corts et al., 2014; Atif et al., 2016; Meng et al., 2017; Ugrinović et al., 2018*). However, some of these materials or their mixtures have unsuitable mechanical and/or chemical properties. With the addition of natural zeolites, enriched zeolites, or synthetic zeolite-like materials of certain traits to growing mixtures, the problem with unsuitable mechanical and/or chemical properties could be solved, but there is a need to more precisely determine the amount and type of fertilizers/nutrients to be added to achieve optimal results.

Natural zeolites are hydrated aluminosilicate minerals of alkali and alkaline earth metal cations with a specific crystalline structure and open cavities that give it a large internal and external surface area (*Šupić et al., 2018*). Zeolites possess remarkable physical and chemical properties, which include releasing and retaining water in a reverse way, adsorbing molecules that act as molecular sieves, and replacing their constituent cations without structural change. Some results emphasize their role in stored-pest management, as inert dust for different purposes such as carriers in the pesticides and fertilizers. Also, it can be used as a soil/substrate mixture amendment, animal feed additives, mycotoxin binders and food packaging materials (*Damjanović et al., 2005; Zoranović et al., 2009; Kljajić et al., 2011; Eroglu et al., 2017; Ugrinović et al., 2018*). Natural zeolites possess many suitable properties, however, the most useful ones in agriculture are cation exchange, absorption, and sorption of plant nutrients and water, as well as the capability of its gradual release (*Mojić, 2006; Križak et al., 2014*).

In the Republic of Serbia, there are more than ten different zeolite deposits with more than 10 million tonnes of reserves. High-quality zeolite deposits are located on the Fruška Gora mountain (Beočin), near Kruševac (Jablanica 1), near Brus (Igroš) and Vranjska Banja (Zlatokop and Toponica) while there are also a few other deposits with medium to low-quality zeolites (*Simić et al., 2014*). At the moment only the Igroš and Jablanica-1 deposits are exploited.

During the last decade of the 20th century, Enriched Zeolites (ZeoPlant™) from Vranjska Banja deposit were widely used in experiments and for vegetable seedling production with excellent results (*Damjanović et al., 1994; Marković et al., 1994; Damjanović et al., 2005; Damjanović et al., 2006).* According to some earlier experiments performed in the Institute of vegetable crops in Smederevska Palanka, as well as the experience of the Institute's senior researchers, the addition of zeolites at about ¼th of the substrate volumetric ratio significantly improves the growth of tomato and pepper seedlings with the best cost-effective result (*Damjanović et al., 1994, Damjanović et al., 2005, Damjanović et al., 2006, Ugrinović et al., 2018*).

After the governmental and political transition in Serbia in late 2000, and a social property transformation a few years later, due to negligence, administrative and bureaucratic problems, Nemetali Company from Vranjska Banja stopped ZeoPlant™ production and closed the mine. Gradually, the lack of the product on the market could be felt, as well as the lack of tidy zeolite ore, used as a raw material for its production.

Currently, the National list of registered plant nutrition products and soil enhancers of the Republic of Serbia includes three registered zeolite-based fertilizers/soil enhancers which are also suitable for organic production (*MAFWM, 2021*).

This study aimed to evaluate different methods and organic or mineral fertilizers used for natural zeolite enrichment, via testing the biological nutritional value of prepared substrate mixtures on lettuce seedlings in the conditions of a controlled environment (greenhouse).

MATERIALS AND METHODS

A series of trials were set up in the experimental greenhouse of the Institute for Vegetable Crops, Smederevska Palanka, located at the institute's experimental field (44°22' N, 20°57' E, 102 m above sea level), during 2016. The greenhouse is equipped with a ventilation system, water supply installation, additional heating system, shading nets, fixed tables, and other necessary accessories to meet the demands of experimental work.

In early 2016 (March 13th), a preliminary experiment was performed. It included ZeoPlant™, Enriched zeolites produced in the Vranjska Banja, Nemetali company, and KTS 1 Klasmann Deilmann company commercial substrate. Their mixtures were examined in different proportions: 1) 0% of ZeoPlant™ and 100% of KTS 1 substrate, 2) 5% of ZeoPlant™ and 95% of KTS 1 substrate, 3) 15% ZeoPlant™ and 85% of KTS 1 substrate, 4) 25% ZeoPlant™ and 75% of KTS 1 substrate, 5) 35 % of ZeoPlant™ and 65 % of KTS 1 substrate and 6) 45% of ZeoPlant™ and 55% of KTS 1 substrate and 7) 55% of ZeoPlant™ and 45% of KTS 1 substrate. The pure commercial substrate was used as a control treatment (1). Styrofoam containers with 104 cells were filled with these mixtures. Three seeds of lettuce (*Lactuca sativa* L. var. *Neva*, Institute for Vegetable Crops, Smederevska Palanka) were sown in every single cell. The trays were regularly watered. After the lettuce sprouts emerged, each cell was left with one plant and others were removed manually. Pest and disease presence was not recorded and apart from watering no other additional care took place until sampling. Also, no symptoms of phytotoxicity were recorded. After 50 days, average samples were collected from the inner cells of the trays. Each sample consisted of 10 plants carefully cleaned and measured using a technical scale.

At the end of March (28th), the second experiment was set up with the same parameters, except the Pirotski peat was used instead of the commercial substrate (KTS 1) to prepare mixtures with ZeoPlant™. Pirotski peat has good chemical and relatively good mechanical properties but if compared with the commercial substrate it has lower porosity and mild water retention.

The final experiment was set up on October 3rd, 2016. Pirotski peat and natural zeolites provided from the Igroš tuff deposit, near Brus (Kopaonik mountain) were used. Basic chemical properties, shown in Table 1, were achieved using standard methods and materials according to national legislation and procedures (*Džamić et al., 2006; Republic of Serbia, 2009; Republic of Serbia, 2010*).

Natural zeolites were ground down and sieved twice through the sieves of different diameters (2,0 mm and 5,00 mm) to form the gravel-like material with uniform size particles. The prepared material was treated with different solutions according to the following procedure. Four plastic barrels (50L volume) were filled with 20 kg of mechanically prepared zeolites each, and then mixed and sprayed simultaneously until reaching saturation with different solutions a) 3% AN – MAP (1:1 v/v) water solution (EZa) and b) 4 % water-soluble fertilizer (NPK 20:20:20) solution (EZb). Because of coarse particles, certified organic fertilizer c) 900 g DCIM ECOMIX (NPK 7:7:10) (EZc), and d) 400 g mineral fertilizer (NPK 15:15:15) (EZd) were ground and poured into water (10L pots) and that liquid was used to soak zeolites in the other two barrels. Manual sprayer (7L size) and plastic pots (10L) were used for the above-mentioned tasks.

ZeoPlant™ and four enriched zeolites were mixed with Pirotski peat in 1:3 ratio and result in one control treatment and 4 (enriched) treatments:

- 25% ZeoPlant™ + 75% Pirotski peat - (Control)
- 25% Enriched Zeolites (*EZa*) + 75% Pirotski peat - (A)
- 25% Enriched Zeolites (*EZb*) + 75% Pirotski peat - (B)
- 25% Enriched Zeolites (*EZc*) + 75% Pirotski peat - (C)
- 25% Enriched Zeolites (*EZd*) + 75% Pirotski peat - (D)

Three polystyrene trays were filled with each of these mixtures (15 trays in total), and the same procedure described above, in relation to sowing, watering, seedlings lead up and nursing was repeated. The third experiment was performed without additional heating. After 8 weeks, the average samples consisted of 20 plants, taken randomly from inner tray cells and the examined traits were collected. Plant height was measured by a plastic ruler. The number of leaves was obtained by counting and a technical scale was used to measure the plant mass. All data is statistically processed in StatSoft Inc. STATISTICA, version 8.0 (2007). Statistical data processing implied one-way analysis of the variance (one-way ANOVA) and the comparison of mean values with the LSD test (least significant difference) at the level of significance $P \leq 0,05$.

Table 1. – Chemical properties of Natural zeolites (Igroš deposit near Brus), commercial Zeolite based Soil Enhancer (SE ZeoPlant™) and Pirotski peat

properties	Natural zeolites	Zeolite based SE	Pirotski peat
pH(H_2O)	n.a.	7.87	n.a.
pH(KCl)	n.a.	n.a.	5.7
Organic matter (%)	< 0.5	n.a.	65.24
N (%)	n.a.	0.947	3.157
P_2O_5 (%)	0.09	1.074	0.67
K_2O (%)	0.923	1.19	0.14
SiO_2 (%)	63.2	61.47	5.68
Al_2O_3 (%)	13.23	12.6	5.25
Fe_2O_3 (%)	2.65	2.33	0.94
CaO (%)	5.25	5.61	2.84
MgO (%)	1.36	1.057	0.73
Na_2O (%)	1.38	1.08	0,1
SO_3	n.a.	n.a.	5.47
TiO_2 (%)	0.23	n.a.	0.001
Cu (mg/kg)	20	n.a.	n.a.
Cd (mg/kg)	2.5	< MPV	< MPV
Pb (mg/kg)	45	< MPV	< MPV
Co (mg/kg)	30	n.a.	n.a.
Zn (mg/kg)	53	n.a.	n.a.
Cr (mg/kg)	20	n.a.	n.a.
As (mg/kg)	<50	< MPV	< MPV

n.a. – not available; MPV – maximal permited values (Republic of Serbia, 2009)

RESULTS AND DISCUSSION

According to the results of the first and second preliminary experiments, all treatments showed higher values of plant biomass compared to control (KTS1 commercial substrate or Pirotski peat, without added ZeoPlant™; the results are only partially presented in Figure 1). The mixture containing 55% of ZeoPlant™ mixed with commercial substrate showed the highest value of fresh plant mass, significantly higher compared to mixtures containing commercial substrate and 25%, 35%, or 45 % of ZeoPlant™ as well as mixtures containing Pirotski peat and high amounts of ZeoPlant™ (35%, 45 %) but without significance compared to treatment containing the highest amount of ZeoPlant™ (55%) and Pirotski peat. However, the difference among the six mentioned treatments was not significant. Since the Pirotski peat is a raw material, without added plant nutrients, weaker plants growth is expected, especially on treatments with less enriched zeolite content. The absence of a statistically significant difference between treatments with 25%, 35% and 45% of enriched zeolites indicates the absence of the need to increase the share of enriched zeolites in substrates for lettuce production.

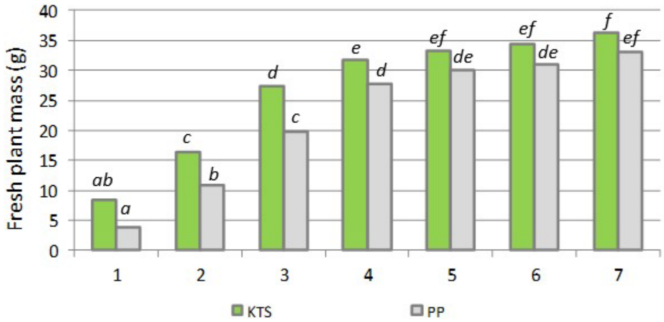

Fig. 1. – Fresh plant mass (g) for different substrate mixtures (KTS – Klasmann Deilmann or PP- Pirotski peat) containing different amounts of ZeoPlant™ (1 – 0%, 2 – 5%, 3 – 15%; 4 – 25%; 5 – 35%; 6 – 45%; 7 – 55%)

In accordance with the results of preliminary experiments, in the final experiment, only the 1:3 volumetric ratio mixture was tested and the tested mixtures showed variations of examined traits (Table 2).

Table 2. – Mean squares (MS) from ANOVA for the analyzed lettuce transplant traits

Effect	Degrees of freedom	Plant height (cm)	Number of leaves	Plant mass (g)
Treatment	4	3.265*	0.3123*	39.69*
Error	10	0.325	0.0947	3.80

**significant at the 0.05 levels of probability, respectively*

The average values of lettuce plant height, number of leaves, and fresh plant mass for examined treatments i.e. substrate mixtures consisting of different enriched zeolites (A, B, C, and D) and ZeoPlant™ (Control) are shown in Table 3.

Table 3. –Average values of lettuce traits for different enriched zeolite (A, B, C, and D) and ZeoPlant™ based substrate mixtures (Control)

treatments	plant height (cm)	number of leaves	plant mass (g)
Control	11.427 [a]	8.4 [a]	33.053 [a]
A	9.993 [b]	8.167 [abc]	26.11 [b]
B	9.76 [b]	7.733 [bc]	25.28 [b]
C	8.503 [c]	7.667 [bc]	23.48 [b]
D	10.16 [b]	8.233 [ab]	26.567 [b]

Values within the same column followed by the same letter do not differ significantly at the 0.05 level of probability, according to the LSD test

Plant height varied from 8.503 cm (treatment C) to 11.427 cm, recorded on ZeoPlant™ based mixture. In the control treatment, the plant's height was significantly higher than in the case of every other mixture. However, between mixtures containing mineral fertilizers and the mixture containing zeolites enriched with organic fertilizer, a significant difference was also recorded. Many experiments performed on the other vegetable species showed the superiority of ZeoPlant™ soil enhancer (*Damjanovic et al., 1994; Marković et al., 1994; Damjanović et al., 2005; Damjanović et al., 2006.).* On the other side, according to *Ugrinovic et al. (2018)*, natural zeolites mixed with green waste compost and vermicompost showed the same growth improvement. Our results suggested that the content of particular nutrients or their availability in the tested EZ was probably below the values of the ZeoPlant^{TM} soil enhancer. Also, weak growth recorded for the mixture containing organic fertilizer as a natural zeolite enhancer can be explained by slower mineralization during the cold weather during lettuce seedlings' growing season.

The highest value of the number of leaves trait was recorded on the mixture containing ZeoPlant^{TM} (8.4), but two of the mixtures with enriched zeolites (A and D) did not differ significantly. Among the enriched zeolite treatments, a significant difference was recorded between treatment C and all other EZ treatments. There is a noticeable difference in favor of zeolites enriched with mineral fertilizers over the treatment with the organic fertilizer for this trait, too. The number of leaves is a trait that can be linked to the speed of development. It is well known that due to the lack of some macro and microelements, some development phases can slow down (*George, 2009; Zdravković et al., 2012*). In addition, natural zeolites adopt cations of macronutrients and microelements by physical forces, making them inaccessible to plants in some cases (*Mojić, 2006*). The aforementioned fact, combined with the property of organic fertilizers to release nutrients slowly, probably contributed to the lack of some macro or microelements in a given growth period.

The average fresh plant mass ranged from 23.48 g (Treatment C) to 33.053 g (Control). The plants grown in substrate mixtures with ZeoPlant^{TM} had significantly higher fresh mass than those grown on different substrate mixtures containing enriched zeolites (A, B, C, and D). The differences between treatments containing enriched zeolites were not significant irrespective of whether the zeolite enrichment was performed by mineral fertilizers or organic fertilizers. In contrast to the results obtained, many authors noted significant differences between treatments on other plant species (*Marković et al., 1994; Damjanović et al., 2005; Damjanović et al., 2006; Ugrinovic et al., 2018*).

CONCLUSIONS

In our study, the best results were achieved using the ZeoPlant^{TM} soil enhancer. According to the results of two preliminary trials, in the case of lettuce seedlings, the optimum amount of the zeolite-based enhancer in the substrate mixture is about 25% of the volume. On the basis of the third experiment, it can be concluded that natural zeolite enrichment should be performed using higher doses or concentrations of mineral or organic fertilizers. For enrichment of natural zeolites intended for the winter lettuce production, priority should be given to mineral fertilizers over organic fertilizers, because during the colder months the mineralization of organic matter is slowed. The experiments on lettuce should be continued by improving the two best-performing treatments (A and D), as well as on other test plants.

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