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ORIGINAL ARTICLE

Use of coal industry wastes and zeolitic tuffs to increase the bio-productivity of agro-landscapes

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ABSTRACT
The paper presents materials on the study of the effect of the complex fertilizer (zeolite + brown coal) on the development of a test plant (barley). The aim of the work was to study the possibility of improving the agrochemical and biological properties of the soil under the influence of complex fertilizer, the assessment of expediency and its long-term operation. Both natural zeolite (clinoptilolite) and its modified forms were used in the study. Barley was used as a test culture.
Key words: *zeolite, brown coal, humic substances, germination energy, germination capacity.*

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INTRODUCTION

To solve the problem of providing the population with food, one of the most important points is to increase the yield of ecologically safe agricultural products and to develop new alternative methods for improving soil fertility [1,2]. The preservation and improvement of soil fertility, the improvement of the supply of plants with mineral nutrition elements, which are the basis for obtaining high stable yields, are associated with scientifically based systems for the use of mineral and organic fertilizers. The growth and development of the plant is subject to the laws of Shelford Laws of Tolerance [3]. According to the first law, the plant grows and develops until the deficient factor is sufficient. According to the second law, the excess of any factor can adversely affect the plant or the soil. The results of studies of increasing the yield of agricultural products by introducing organo-zeolite fertilizers into the soil [4,5] are known. Among organic fertilizers, a group of organic substances of natural origin, known as humic fertilizers, stands out [6]. The content of humus in the soil is important not only for its fertility [7].

Humus contains up to 99% of soil nitrogen, 60% of phosphorus, up to 80% of sulfur and other trace elements. But these nutrients are inaccessible to plants and they become food for them only after decomposition, when carbon dioxide, which is the source of their air supply, is released [8]. Humic substances affect the plant directly or indirectly. Under the influence of humic substances, the permeability of cell membranes changes, the activity of many enzymes, respiration, synthesis of proteins and carbohydrates increase. They have a positive effect on the mineral nutrition of plants, water exchange, increasing the content of chlorophyll, the productivity of photosynthesis and transpiration. All this ultimately leads to increased growth, increased yield, accelerated ripening and improved product quality [9]. The indirect effect is associated with the improvement of the water-physical properties of the soil, the activation of microflora, the effect on the migration of nutrients, the increase in the utilization rate of mineral fertilizers, the binding of toxic agents (pesticides, herbicides, heavy metals, etc.). Along with this, humic substances have a direct deep and diverse effect on plant growth processes, i.e. regulate them [10].

The practice of using humic preparations obtained from brown coal in plant cultivation, and numerous comparative studies [11,12] indicate that humic substances from brown coal are similar in their properties to soil humic acids, at least in terms of participation in the soil-forming process and in a stimulating effect on plant growth and development. Humic substances have the property of binding toxic substances, such as heavy metal salts, radionuclides, aromatic hydrocarbons and other compounds that appear in the process of industrial and other human activities, which is their main protective or environmental property. The ecology polluters connected in this way are "preserved" and do not enter the organisms of living beings and humans [8,13]. The highest content of humic substances is in brown coal, peat and sapropel.

Coal deposits are an almost unlimited source of humic substances, which is a unique product that plays a key role in the formation and functioning of the soil and can be used to solve many agricultural and environmental problems.

Zeolites are an extensive group of minerals, which is the sixth in the stratosphere in terms of prevalence and mass, after feldspars, quartz, mica, clay minerals and carbonates. Out of all (more than 30) the mineral zeolites known in nature, only a few meet the requirements for practical use, in particular, they form large, almost monomineral concentrations and at the same time, have corresponding useful properties: high adsorption capacity, cationic capacity and acid- and heat resistance [14,15]. Zeolites are nanoporous crystalline solids and have a frame structure with alumina-silicon-oxygen base [16]. Zeolites that are currently of practical importance include clinoptilolite, mordenite, and shabazit [17].

Clinoptilolite tuffs have an exchange capacity of about 2 $mgmol^{-1}/g$ and a zeolite water content of about 15%. Due to the secondary porosity of rocks, total moisture capacity reaches 45%. Therefore, the introduction of clinoptilolite into the soil significantly increases its moisture and ion-exchange capacity. A distinctive feature of ion exchange on clinoptilolite is a highly expressed selectivity towards such massive cations such as K^+ and NH_4^+, which are the main active elements of mineral fertilizers. This determines their constant transition to the soil, delays the removal of ground waters and rainwaters and increases the efficiency of the fertilizer [17-19]. The use of prolonged action fertilizers with the gradual release of nutrients is a promising direction in technology of agricultural crops, as it has a number of significant advantages compared with the use of traditional mineral fertilizers [20,21].

High exchange capacity, selectivity to potassium and ammonium ions, as well as high rates of exchange reactions allow clinoptilolite to be considered as a soil sorption-type soil improver. When using zeolite tuffs as artificial soil, it is necessary to pre-saturate clinoptilolite with nutrient components. In particular, potassium-ammonium form of clinoptilolite can be used for these purposes. The experimentally established high biological activity of the ammonium form, expressed in a significant increase in yield and protein content in the grain, makes it possible to consider the clinoptilolite in the ammonium or potassium-ammonium form as a very effective long-acting fertilizer [18,22,23]. Clinoptilolite has a significant effect on the distribution of microelements in the soil-plant system, drastically reducing the content of toxic metals in the green mass and grain. The duration of the protective action of clinoptilolite is associated with the process of self-cleaning, due to the periodic entry of contamination. This property of clinoptilolite acquires particular importance when used in crop production of composts, irrigation water and fertilizers containing toxic substances [24-27].

The aim of the work was to study the possibility of improving the agrochemical and biological properties of the soil under the influence of complex fertilizer: modified zeolite + brown coal, its influence on some biometric indexes of test cultures.

MATERIAL AND METHODS

In this work, Brown coal (from the Akhaltsikhe deposit of Georgia) and natural zeolite –clinoptilolite of sedimentation origin (from the Tedzami deposit, the Khandaki district of Georgia) modified with potassium and ammonium ions were used as a source of organic matter to obtain complex fertilizer.

X-ray fluorescence spectroscopic analysis of brown coal showed that the content of toxic elements does not exceed the maximum permissible norms (MPN).

Modification of the zeolite with ammonium and potassium cations was carried out by treating the initial natural clinoptilolite with 0.1N solutions of NH_4Cl and KCl, respectively. Untreated brown coal was used as the second component of the fertilizer [28].

The experiment was carried out on meadow-brown soil type, with a weak alkaline reaction of an aqueous solution (pH = 7.3-7.9). The soil is characterized by a low content of humus from 1.93 to 2.90%, and its granulometric composition is classified as heavy loamy soil [29].

The experiment was carried out in vegetation vessels, in five variants, each in three replications. Barley of "Alaverdi-1"variety was used as a test plant to test the fertility of substrates. Sowing of this culture in substrates was carried out repeatedly (5 sowing), in permanent circulation, i.e. in the variant of monoculture, which most aggressively affects the fertility of the soil, causing the so-called "soil fatigue" [30].

In the first case, the soil was used as a reference (comparison object). In the second case, the substrate was prepared by mixing finely ground natural, unmodified zeolite + soil. The third version is soil + zeolite modified with potassium and ammonium cations. The fourth version of substrate was made by using raw brown coal and natural zeolite (without soil), fifth - brown coal + zeolite modified with potassium and ammonium cations (without soil).

Before the experiment began, the sowing qualities of barley seeds, germination capacity (91%) and germination energy (85%) were determined. Germination energy was determined in Petri dishes on damp filter paper placed in a thermostat (at 20°C) after three days and germination capacity – on the seventh day. The number of normally germinated seeds under optimal conditions established by the standard for each culture, shown in percentage is considered under the germination capacity of seeds. Germination energy was also determined. The germination energy, characterizing the intergrowth in unison of seed germination, is the number of normally germinated seeds for a certain period established for each crop, shown in percentage [31].

Germination capacity and seed germination energy are the most important indexes of their sowing qualities. Seeds with good germination capacity and high germination energy with normal agricultural technology always give friendly and full-fledged seedlings.

Seeds of barley in the amount of 50 pieces were sown on each substrate (vessel). After 30 days from sowing, the sprouts together with the roots were carefully removed from the substrate, washed with distilled water, dried at 75°C until a constant weight was reached. Dry plant biomass per one vessel was determined by weighing, taking into account both the whole plant (total underground and surface part) and the root system only.

In total, five sowing were carried out consequently with appropriate processing of the obtained results. The assessment of the expediency of using the developed substrate in plant growing and the possibility of its long-term operation was determined by the method proposed by Bulgarian scientists: the ratio of dry biomass of a plant grown in the first crop to the biomass of plants grown in subsequent crops (respectively, second, third, etc.) [32]. An increase in this index indicates an exhaustion of the soil fertility (in our case a substrate during its exploitation) whereas a decrease indicates an increase in fertility.

RESULTS AND DISCUSSION

The following biometric indexes were determined: germination energy (GE), relative germination energy (RGE), germination capacity (GC), relative seed germination capacity (RSGC). Table 1 shows the arithmetic mean data determined from three replications of each option.

Table 1. The impact of the substrate on the biometric indexes of barley.

biometric indexes	sowing	substrate				
		soil (comparison object)	soil-zeolite	soil-modified zeolite	brown coal-zeolite	brown coal-modified zeolite
GE	1 sowing	70	30	34	36	40
	2 sowing	66	50	55	58	63
	3 sowing	40	82	90	84	95
	4 sowing	34	71	88	76	90
	5 sowing	20	52	60	55	83
RGE	1 sowing	-	-0.57	-0.52	-0.48	-0.43
	2 sowing	-	-0.24	-0.17	-0.12	-0.04
	3 sowing	-	1.05	1.25	1.10	1.37
	4 sowing	-	1.08	1.59	1.24	1.65
	5 посев	-	1.60	2.00	1.75	3.15
GC	1 sowing	76	38	42	52	55
	2 sowing	78	60	64	76	84
	3 sowing	46	86	94	92	99
	4 sowing	40	83	90	87	97
	5 sowing	36	76	85	80	90
RSGC	1 sowing	-	-0.50	-0.44	-0.32	-0.27
	2 sowing	-	-0.23	-0.18	-0.02	0.07
	3 sowing	-	0.87	1.04	1.00	1.15
	4 sowing	-	1.07	1.25	1.17	1.43
	5 sowing	-	1.12	1.36	1.23	1.50

Analysis of the data given in Table 1 indicates that the application of zeolites and brown coal has a positive effect on the germination and germination capacity of barley seeds. The biggest growth in germination capacity and germination energy occurs while using zeolites modified with potassium and

ammonium cations and brown coal during the third sowing. The high bioproductivity of plants grown on a substrate consisted of modified zeolite and brown coal, as compared with bioproductivity on other variants, can presumably be explained as follows: In studies [33,34], it was shown that the cations that are part of zeolites, have the ability to get into ion exchange reaction not only in aqueous solutions, but also in the solid state. Although, the exchange reaction is more slow in this case. Therefore, the following mechanism of ion exchange is assumed in substrates: the NH_4^+ + and K^+ cations from zeolite get into exchange reactions with humic and fulvic acids, forming the corresponding salts, soluble in the aqueous medium. In such condition, these formed organic substances can contribute to the humification of the substrate, as well as their digestibility by plants. On the other hand, the high bioproductivity of this substrate, presumably, can be associated with the formation of a favorable microbial landscape of the soil (biota), promoting plant growth and development, in the system – soil-zeolite-brown coal-plant [35,36].
As we can see from the table, germination energy and germination capacity gradually decrease on the soil (the object of comparison) from the first to the fifth sowing. This is probably due to the exhaustion of the soil. These indicators increase on substrates and on the third crop reach the highest index. An increase in fertility on substrates, containing modified zeolite and brown coal occurs due to these components.
The structure and flexibility of the root system play an important role in improving growth and increasing crop yields. The figure shows plants grown on different substrates.

Figure 1: Plant germination on various substrates:
a) soil (object of comparison); b) soil + zeolite; c) brown coal + zeolite; d) soil + modified zeolite; e) brown coal + modified zeolite.

As we can see from the Figure, the enrichment of the soil with substrates affects the growth of both, the over ground part and the root system of the plant. Al though, this indicator varies on different substrates. The root system develops more on the substrate: soil + zeolite and brown coal + zeolite; the over ground part – on the substrate: soil + modified zeolite. A big difference is shown in case of lignite + modified zeolite. Differences were also noted in the dry mass of plants, both the land part and the root system, which demonstrate an increase in the growth of plants grown on composites with substrates. These indicators are shown on the diagram, which is constructed according to the third sowing. Table 2 shows plant masses on various composites.

Table 2. Plant masses on various composites (g).

Sowing	Mass (g)									
	soil (comparison object)		soil+zeolite		soil+modified zeolite		brown coal+zeolite		brown coal+modified zeolite	
	Root	land	Root	land	Root	land	Root	land	Root	land
I	1.5	1.3	1.8	1.5	1.2	1.0	2.9	2.3	2.3	1.3
II	0.8	1.1	2.3	1.9	1.3	1.2	4.3	2.5	4.5	2.8
III	0.7	0.7	4.5	2.8	4.0	6.0	5.5	5.0	6.5	8.5
IV	0.5	0.6	4.0	2.0	3.5	4.0	5.0	4.3	7.0	8.0
V	0.5	0.5	2.3	1.7	3.0	2.3	4.5	4.0	6.0	6.5

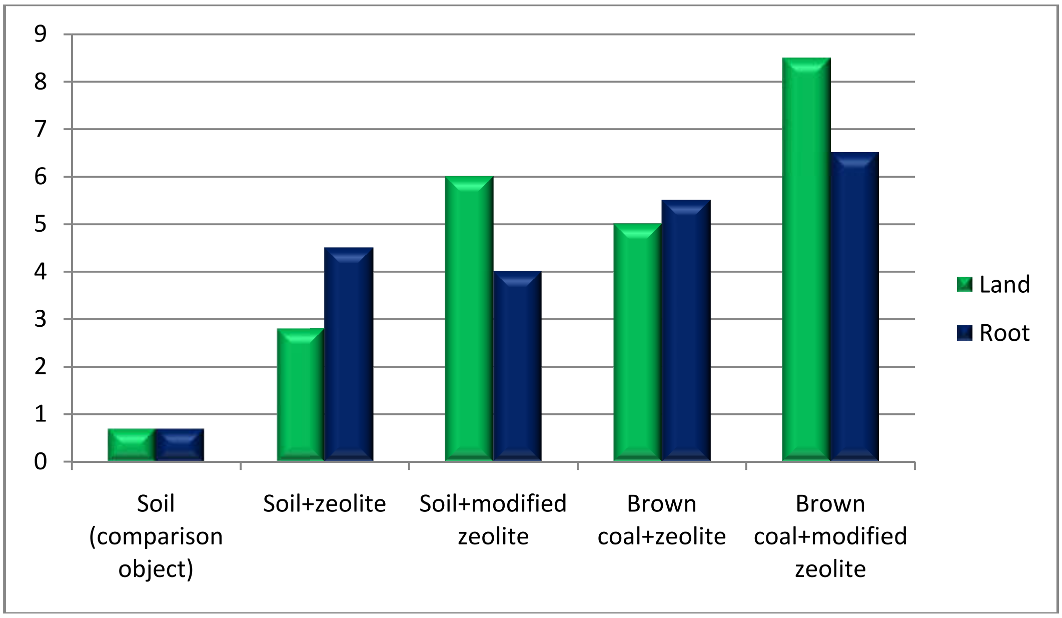

Fig 2. Changes in the dry mass of plants on different composites during the third sowing.

As we know, barley is characterized by an intensive growth of vegetative organs in a short time; In this time, it forms a sufficiently powerful root system and leaf surface. According to tables 1.2 and diagrams, in the third sowing period, seed germination capacity was 99% on the substrate – brown coal-modified zeolite. An increase in the mass of germinated plants was also noticed. Manipulation of the vegetative organism by enriching the soil with biologically active substances is currently very common.

Among the promising methods for increasing the yield and quality of crop production are the composites proposed in the work (zeolite, lignite). They are able to stimulate physiological and biological processes during the germination of crops, which increases the resistance of forming plants to environmental stress factors and directly affects the economically useful traits and productivity of the crops grown. Further studies in this direction are highly relevant: from an environmental point of view, they promote the utilization of substandard coal industry wastes as an organic component of substrates that increase soil fertility**.**

REFERENCES

1. Ivanov A.L. (2007) Priorities and the main directions of agriculture development// Zemledelie, 3, 2-4 (in Russian).
2. Kiryushin V.I. (2013) Problems of minimization of the soil treatment: Prospects of the development and problems of the study// Zemledelie, 7, 3-6 (in Russian).
3. https://ru,wikipedia.org/wiki/shelfordlow
4. Naumkin V.N. (2004) Problem approach in the modern agriculture//Agromir, 5(12) (in Russian).
5. Ivleva A.A. (2016) Methods for Increasing Productivity of Agricultural Crops by applying of Organic-Mineral Fertilizers based on Astrakhan Zeolites. Publications of Research Articles SCI-ARTICLE.
6. Chen Y., Clapp C.E., Magen H., Cline V.W. (1990) Simulation of Plant Growth by Humic Substances: Effect of iron Availability. Understanding Humic Substances. Advanced Methods, Properties and Applications EDS E. Ghabbour, G.Davies. Cambridge, 150.
7. Levin B. V., Ozerov S. A., Garmash G. A., Latina N.B., Garmash H. U. (2015) Raise of Agrochemical Efficiency of Complex Phosphoric Fertilizes at the expense of Humate Additives. Plant Nutrition, #2, 2-8.
8. The concept of production of humus based on brown coal in the Republic of Buryatia (2017), Minsk / www.sw-tech.by.
9. Putkaradze A. (2010) Influence of soil and organic fertilizer treatment differences on soil humus balance and crop yields. Proceedings of the St. Petersburg State University. (18), 79-81 (in Russian).
10. Paul I. (2010) Fixen The concept of increasing the productivity of agricultural crops and the efficiency of using elements of plant nutrition. Plant nutrition: Bulletin of the International Institute of Plant Nutrition, №1, 2-7.
11. Usanbaev N., Namazov Sh., Beglov B., Rahmanjanov U., Eshimbetov A. Obtainment of nitrogen-humic fertilizers based on urea, oxidized brown coal and their IR-spectroscopic study. Universum: Technical science, #9(30), 2016.

12. Putsykin Y., Shapovalov A., Stepanov A., Bodoev H., Kostrikova T. Humic acids, as a special type of organomineral polymers. Agrosynthesis, Applied agricultural technologies, www.agrosintez.ru/ru/articles/article_04.ht.
13. Ul'yanova O.A. (2009) Effect of new compound fertilizers prepared from bark and zeolite on the transformation of organic matter of soil. J. Fertility, #2, 23-25.
14. Razmakhnin K., Khatkov A. (2011) Modification of the properties of zeolites for the purpose of expanding the areas of their application. Scientific and Technical Journal: Mining Information and Analytical Bulletin, 246-252.
15. Coombs D.C. (1971) Present status of zeolites facies // Molecular Sieve zeolites. - j. Amer. chem. Soc., Wash.D.C., 317-327.
16. Radovski V.S., Astapova E.S., Filimonov A.V. (2011) Formation of physicochemical properties of the zeolite-nanoparticlesystem during mechanical activation. Scientific and technical statements of SPBSTU. Physics and Mathematics science 4`, 16-24.
17. Danilov K.P. (2009) Effect of zeolites-containing fertilizer on the yield of zucchini. J. Fertility, #3, 15.
18. Chelishchev N.F., Bernstein B.G., Volodin V.F. (1987) Zeolites - a new type of mineral raw materials, M .: Nedra, 176.
19. 19.Andronikashvili T.G., Urushadze T.F., Eprikashvili L.G. (2009) Zeolite-containing substrates a new way from plant growing in plant production. J. Ann. Agrar. Sci. 7, 14-45. (in Russian).
20. Perminova V., Zhilin D.M. (2004) "Humic substances in contact of green chemistry, coll. articles Green chemistry in Russia. Moscow, 146-162. (in Russian).
21. Eskov A.I., Novikov M.N. (1998) Problems of production and use of organic fertilizers. Agrochemical Herald. 4, 29-32. (in Russian).
22. Andronikashvili T.G., Urushadze T.F. (2008) Application of zeolite-containing rocks in plant growing // Agrochemistry, 12, 63-79.
23. Buondonno A., Coppola E., de'Gennaro B., Leone A.P., Letizia A. and Colella C. (2010) Morpho-structural and chemical-physical properties of soil ped aggregate models by interaction of phillipsite-chabazitic or clinoptilolitic tuffs with different organic matter. 8th International Conference of the Occurrence, Properties, and Utilization of Natural Zeolites, Sofia, Bulgaria, 10-18 July, 52-53.
24. Leggo P.J. (2014) The Organo-Zeolitic-Soil System: A Comprehensive Fertilizer. International Journal of Waste Resources, v.4, issue 3.
25. Febles J.A., Núñez G.M.S. (2010) Natural zeolite in the industry of fertilizers – agronomic results. 8th International Conference of the Occurrence, Properties, and Utilization of Natural Zeolites, Sofia, Bulgaria, 10-18 July, 86-87.
26. Andronikashvili T., Zautashvili M., Eprikashvili L., Burkiashvili N., Pirtskhalava N. (2012) Natural Zeolite – one of the Possibilities of transition from "Chemical" to Biological Agronomy. Bulletin of the Georgian National Academy of Sciences, v.6, #2, 111-118.
27. Eprikashvili L.G., Zautashvili M.G., Dzagania M.A., Pirtskhalava N.V., Burkiashvili N.O. (2008) Influence of synthetic zeolite on wheat seed germination. Proceedings of the Georgian National Academy of Sciences, Chemical series, v.34, #1, 103-106.
28. Urushadze T. (1997) The main soils of Georgia // Tbilisi, Metsniereba, 267.
29. Belitsyna G.D., Vasilevskaya V.D. (1988) Soil Science (Soil and Soil Formation), Part 1 // M.: Higher School, 400.
30. De Gennaro M., Langella A., Colella C., Coppola E., Buandanno A. (1997) Proceedings of the Sofia Zeolite Meeting'95, Pensoft, Sofia-Moscow, 93-100.
31. Manolov I., Stoilov G. (1995) Changes in Nutritional Properties of Zeolite Substrates During Their Exploitation // Natural Zeolites - Sofia'95 Pensoft, Sofia-Moscow, 83-92.
32. Tsitsishvili G.V., Avaliani K.E., Adolashvili M.G. (1968) Method for obtaining ion-exchange zeolites // Certificate of Authorship SSR 223784.
33. Andronikashvili T., Urushadze T., Eprikashvili L., Gamisonia M., Nakaidze E. (2008) Towards the biological activity of the natural zeolite – clinoptilolite – containing tuff. Bulletin of the Georgian National Academy of Sciences, v.2, #3, 99-108.
34. Eprikashvili L., Tsitsishvili V., Zautashvili M., Kordzakhia T., Dzagania M., Pirtskhalava N. (2015) Influence of the ground-free substrate on the biometric parameters of bean and barley germination. Bulletin of the Georgian National Academy of Sciences, v 9, # 1, 139-144.
35. Eprikashvili L., Zautashvili M., Kordzakhia T., Pirtshkalava N., Dzagania M., Rubashvili I., Tsitsishvili V. (2016) Intensification of Bioproductivity of Agricultural Cultures by Adding Natural Zeolites and Brown Coals into the Soil. Annals of Agrarian Science, v.14, 67-71.
36. Eprikashvili L., Pirtskhalava N., Zautashvili M., Kordzakhia T., Dzagania M., Tsintskaladze G. (2018) Use of Georgian non-traditional agricultural resources in agriculture. International Journal of Advanced Research (IJAR), 6(1), 1408-1415.

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