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Plant Growing

Anionic Zeolite Nanomaterial – Environmentally Safe Complex Fertilizer with Prolonged Action

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The development and implementation of effective and cost-effective environmental technologies is one of the priority problems in Georgia for the rehabilitation of soil fertility and natural vegetation cover. The paper proposes a new method for nanomodification of natural zeolite - clinoptilolite, based on the introduction of the appropriate salt into the structure of the zeolite so that the resulting material does not lose its zeolite structure and acquires both cation-exchange and anion-exchange properties. Some amount of ammonium dihydrogen phosphate ($NH_4H_2PO_4$), potassium nitrate (KNO_3) and cations mixed with them (Fe, Ca, Mn, Zn, Mg, Cu, Mo, Co, Sn) were introduced by fusion method into the clinoptilolite structure. Only the amount of ammonium dihydrogen phosphate changed, while the amount of potassium nitrate (KNO_3) and cations remained unchanged. Accordingly, zeolite nanomaterials of various composition, structure and properties were obtained, which were studied by the methods of chemical, IR spectroscopic and X-ray diffractometric analyses. The obtained zeolite nanomaterials as fertilizers of complex composition and long-term action were used to study their effect on wheat productivity both in the open field and in laboratory conditions. Zeolite nanomaterials of three different compositions were studied.

Natural zeolite, zeolite-anionic form, nanomodified, I.R. spectroscopic, agriculture

A research in the field of application of zeolites revealed a wide range of their use in agriculture. Due to the rich content of natural chemical elements, zeolite is an excellent mineral supplement. Against the background of low soil fertility and unfavorable climatic conditions, it is embarrassing to get a full harvest of agricultural crops without the use of fertilizers. However, the deficit and high cost of mineral fertilizers do not allow their widespread use; meanwhile, the introduction of high doses of mineral fertilizers is not justified [1, 2]. The problem of plant mineral nutrition is still far from being solved for two main reasons. The first reason is that plant nutrition requires a complex intake of both macro- (N, P, K, Ca, Mg, S) and microelements (Fe, Cu, Zn, Co, Mo, B, etc.). The second reason is the large heterogeneity of environmental factors (composition and properties of soil, moisture, temperature, etc.). Both factors largely determine the elements required for plant nutrition, as well as their amount. Therefore, in practical work, it is necessary to take these factors into account. The influence of mineral fertilizers on soil fertility is small, since most nitrogen fertilizers are either washed out or evaporated after application, while most phosphorus fertilizers are easily absorbed into the soil and turn into poorly soluble forms and the utilization rate of such fertilizers is very low, no more than 15-25% [3-6].

The molecular-sieve and adsorption properties of zeolites were used to fill their structure with anionic substituents. The resulting anionic forms of zeolites are very similar to ionic compounds. Salt cations and anions are probably located both in the intracrystalline structure and in the mesopores of natural zeolite [7].

Materials and Methods

To obtain a balanced nutrition for the plant, a new zeolite nanomaterial is proposed - a fertilizer of a complex composition based on clinoptilolite, based on the introduction of the appropriate salt into the zeolite structure, the resulting material does not lose its zeolite structure and acquires both cation-exchange and anion-exchange properties. A certain amount of ammonium dihydrogen phosphate ($NH_4H_2PO_4$), potassium nitrate (KNO_3) and cations mixed with them (Fe, Ca, Mn, Zn, Mg, Cu, Mo, Co, Sn) were fused into the clinoptilolite structure. The amount of ammonium dihydrogen phosphate was variable. Zeolite nanomaterials of various

Table 1. Chemical analysis of the composition of zeolite fertilizer before and after use

Fertilizer ions	Zeolite fertilizer in different proportions (ion content)					
	1:1		1:2		1:3	
	Initial (before the use)	After the use	Initial (before the use)	After the use	Initial (before the use)	After the use
SiO_2	5.95%	35.24%	7.55%	36.16%	6.08%	25.04%
Al_2O_3	2.27%	8.30%	2.38%	9.48%	1.90%	6.73%
P_2O_5	34.17%	18.97%	33.8%	13.9%	38.2%	35.4%
K_2O	10.8%	5.5%	13.5%	5.5%	11.1%	8.6%
NH_4^++NO_3^-	2.40%	–	2.46%	–	2.46%	–
Fe_2O_3	3.2%	3.1%	1.08%	4.7%	0.9%	7.8%
CaO	1.4%	9.6%	1.5%	6.8%	1.2%	3.5%
MnO	0.04%	0.1%	0.04%	0.2%	0.03%	0.13%
Na_2O	0.13%	0.13%	0.13%	0.13%	0.13%	0.13%
MgO	0.02%	1.1%	0.02%	1.9%	0.02%	0.2%
Zn	59.50ppm	-	52.60ppm	-	43.50ppm	-
Cu	46.40ppm	-	30.10ppm	-	26.50ppm	-
Mo	13.90ppm	-	14.70ppm	-	13.30ppm	-
Co	5.40ppm	-	3.50ppm	-	3.00ppm	-
Sn	1.30ppm	-	1.20ppm	-	1.09ppm	-

composition, structure and properties were obtained, which were studied by methods of chemical, IR spectroscopic and X-ray diffractometric analysis. The ratio of zeolite and ammonium dihydrogen phosphate salt was 1:1, 1:2, and 1:3, respectively, and the amount of potassium nitrate remained unchanged in all three cases. Chemical analysis of the samples was carried out on a Spectroscout XEP-04 analyzer (Germany). The analysis results are presented in Table 1.

As can be seen from Table 1, a certain amount of cations and anions is included in the zeolite structure. The detection of ammonium, nitrate, and phosphate ions in zeolite nanomaterials treated with the corresponding salts, as well as the change, was monitored by chemical analysis and by IR spectroscopy and X-ray diffractometry methods.

X-ray diffractometric analysis was performed on Dron-4 (Russia). The experiment showed that the ingress of an amorphous salt mass into the structure of clinoptilolite as a result of melting causes some deformation of its structure. It seems that melting causes desorption of water from the zeolite channels, as well as the migration of cations, these places are occupied by ammonium dihydrogen phosphate and the structure of the zeolite partially changes.

IR spectrometric analysis of the samples was carried out on an Agilent Cary 630 FTIR spectrometer in the range of 350-5000 cm^{-1} (USA). The IR spectra clearly show peaks corresponding to NH_4^+, NO_3^-, and PO_4^{3-} ions, included in the structure of the zeolite, at 1402, 1387, 1292, 925, 825, 547 cm^{-1} [7, 8]. After nanomodification, the structure of the zeolite practically does not change. This is indicated by the presence of bands of both bending (449 cm^{-1}) and stretching (1117 cm^{-1}) vibrations of the Si - O - Si (Al) bond in the infrared spectrum of zeolite [9]. Removal of anions from the zeolite structure by washing with water occurs gradually; at the end, the zeolite structure returns to its original form, as indicated by the maximum decrease in the intensity of the bands at 1402, 1387, 1292, 925, 825, 547 cm^{-1}, which correspond to NH_4^+, NO_3^- and PO_4^{3-} ions.

Results and Discussions

The introduction of zeolites into the soil, in addition to improving its structure, increasing aeration, constantly retaining moisture, enriching it with microelements, etc., have unique adsorption and molecular sieve properties. The introduction of zeolites into the soil in combination with other components provides a gradual supply of useful components to the plant and thereby, prolong their action [8, 10-14]. To study the effect of the obtained zeolite fertilizer of complex composition on types of agricultural crops, a variety of winter wheat from Germany, Amicus, was chosen. The experiments were carried out in the field (open ground) (Georgia, Gurjaani region, the village of Bakurtsikhe), as well as in laboratory conditions in growing vessels. At the first stage, substrates were selected for testing in which the proportions of ammonium dihydrogen phosphate and zeolite prepared for fusion (zeolite: ammonium dihydrogen phosphate salt) were 1:1, 1:2.and 1:3, and the amount of potassium nitrate (KNO_3) did not change. The obtained substrates, together with the soil of the experimental site, were introduced both into vegetative vessels and into open ground before sowing. Both variants of the experiment were carried out according to a 5-variant

Table 2. An agrochemical study of the soil

Soil depth, cm	pH	$CaCO_3$,%	Humus,%		Hydrolyzed nitrogen, mg/100g		Absorbable phosphorus, mg/100g		Exchangeable potassium, mg/100g	
			%	Level of provision	mg/100g	Level of provision	mg/100g	Level of provision	mg /100g	Level of provision
0-20	7.76	7.4	3.96	Average	5.6	Low	1.03	Very low	13.5	Low
20-40	7.80	8.2	2.69	Low	4.2	Low	0.68	Very low	11.0	Low

Table 3. Quantitative indicators of culture grown in laboratory and field conditions

Quantitative indicators of culture	Lab-grown, g					Field-grown, t/ha				
	Soil	Soil + zeolite	1:1	1:2	1:3	Soil	Soil + zeolite	1:1	1:2	1:3
Medium weight of colossus	0,82	1.27	1.55	0.63	0.10	2.95	3.25	4.10	3.80	3.00
Weight of dry straw	20.18	25.73	37.45	9.37	2.90	3.30	4.60	5.50	4.20	3.40

Test scheme	Wheat quality indicators in %		
	Protein, %	Raw gluten, %	Fat, %
Fertilizer omitted (test)	10.5	20.2	1.95
Fertilizer 1:1	14.7	35.3	2.07

scheme with a threefold repetition and in full accordance with the accepted agroconditions for carrying out such experiments. Preliminary, an agrochemical study of the soil was carried out (Table 2). As can be seen from the table, the soil of the experimental site has an alkaline reaction (pH 7.76-7.80), the soil is moderately calcareous.

The content of all three main nutrients (N, P, K) is low; therefore, synthesized zeolite substrates were introduced into the soil. Accordingly, the amount of zeolite substrate required for the field site and for the growing vessels was determined. It should be noted that the coloration of the culture (wheat) grown on fertilized soil was in all cases darker green and had a stronger stem, and the number of ears was much higher than that of plants grown on control variants (clean soil). After harvesting wheat, it was found that both in laboratory growing conditions and in the field, the best results were obtained with zeolite substrates, 1:1 composition. In field conditions, the yield increase was 36.6% compared to the control (clean soil) variant, while under laboratory conditions the yield increase was 26% (Table 3). Of particular note is the improvement in the quality indicators of wheat. Wheat grown using fertilizer obtained in a 1:1 ratio of components has a higher content of protein, fat and raw gluten, which determines its better baking properties (Table 3). After the end of the experiment, a selectively conducted chemical analysis of the spent zeolite substrate was carried out. The results are shown in Table 1. The analysis showed that the remaining amount of potassium and phosphorus in the applied fertilizer is quite large. Thus, the obtained zeolite substrate is characterized by a prolonged action.

Conclusion

Thus, the proposed zeolite nanomaterial can be successfully used as a fertilizer. Anions of phosphoric and nitric acid are introduced into the structure of the zeolite, and their transfer to the soil occurs gradually due to the molecular-sieve properties of the zeolite. Moreover, the structure of the zeolite also acts as a capsule, as a result of which the interaction of PO_4^{3-} - anions with soil ions is minimized; accordingly, the formation of phosphorus ions in the form of insoluble or hardly soluble salts is minimal, which maximizes the efficiency of applying zeolite fertilizers. In addition, nitric acid anions are less likely washed out into wastewater or groundwater and cause less soil contamination. The use of the resulting fertilizer will help limit the environmentally ecological negative impact of conventional mineral fertilizers. In fertilizers of this type, losses of macro- and microelements are minimized. Also, the assimilation of nitrogen by plants and the utilization rate of phosphorus fertilizers increase.

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მემცენარეობა

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**ივანე ჯავახიშვილის თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო*
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ნიადაგის ნაყოფიერების და ბუნებრივი მცენარეული საფარის რეაბილიტაციის მიზნით საქართველოში ეფექტური და ეკონომიურად რენტაბელური გარემოსდაცვითი ტექნოლოგიების განვითარება და დანერგვა ერთ-ერთი პრიორიტეტული პრობლემაა. სამუშაოში შემოთავაზებულია ბუნებრივი ცეოლითი – კლინოპტილოლიტის ნანომოდიფიცირების ახალი მეთოდი, რომელიც დაფუძნებულია ცეოლითის სტრუქტურაში შესაბამისი მარილის შეყვანით, რის შედეგადაც მიღებული მასალა არ კარგავს თავის ცეოლითურ სტრუქტურას და იძენს კატიონმიმოცვლით და ანიონმიმოცვლით თვისებებს. ამონიუმის დიჰიდროფოსფატის ($NH_4H_2PO_4$), კალიუმის ნიტრატის (KNO_3) და მათთან შერეული კატიონების (Fe, Ca, Mn, Zn, Mg, Cu, Mo, Co, Sn) გარკვეული რაოდენობა კლინოპტილოლიტის სტრუქტურაში შეყვანილი იყო შელღობის მეთოდით. იცვლებოდა მხოლოდ ამონიუმის დიჰიდროფოსფატის რაოდენობა, ხოლო კალიუმის ნიტრატისა (KNO_3) და კატიონების რაოდენობა უცვლელი რჩებოდა. შესაბამისად მიღებული იყო სხვადასხვა შემადგენლობის ცეოლითური ნანომასალა. მათი სტრუქტურა და თვისებები შესწავლილი იყო ქიმიური, ი.წ.–სპექტომეტრული და რენტგენოდიფრაქტომეტრული ანალიზით. მიღებული ცეოლითური ნანომასალები, როგორც რთული შემადგენლობისა და ხანგრძლივი მოქმედების სასუქები, გამოყენებული იყო ხორბლის მოსავალზე გავლენის შესასწავლად ღია გრუნტში და ლაბორატორიულ პირობებში. შესწავლილი იყო სამი სხვადასხვა შემადგენლობის ცეოლითური ნანომასალა.

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