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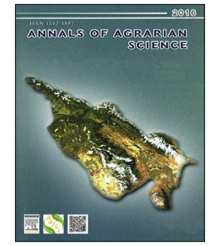

Nanomodified natural zeolite as a fertilizer of prolonged activity

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ARTICLE INFO

Article history:
Received 26 January 2016
Accepted 3 May 2016
Available online 24 May 2016

Keywords:
Zeolite
Nanomaterial
Mineral nutrition
Macroelements
Microelemenats

ABSTRACT

Natural zeolites of sedimentary origin are widely used in agriculture both as individual fertilizer and a mix of mineral and organic fertilizers. Natural zeolites are crystalline nanoporous hydrated aluminosilicates. Fertilizer of prolonged activity enriched with macro- and microelements is obtained by fusing zeolite with dehydrated ammonium using nanotechnological method of modification. The structure and some physical and chemical properties of a novel nanomaterial were studied by the methods of X-ray diffraction, IR-spectroscopy, absorption and thermal analysis. It was shown that the obtained fertilizer may be used in both protected and open grounds.

Introduction

The main factors determining the growth, development and crop yield of plants are light, warmth, water and mineral nutrition. Problems of mineral nutrition and regulation are studied for more than 100 years but the problem is unsolved yet for the two main reasons:

1) Plants need nutrition with complex of macro- (N, P, K, Ca, Mg and S) and microelements (Fe, Cu, Zn, Mn, Co, Mo, B and others) simultaneously. On account of a close mutuality between nutrition elements at the process of nutrition intake, changing amount even of one element in the soil, the delivery of other elements and a nutrition regimen of plants change;
2) Heterogeneity of ecological factors: composition and properties of soils, humidity, temperature, etc., determining considerably the volume of nutrition elements, in which plants need necessarily.

All these factors are taken into consideration in practice and experimental works [1].

It is already known that organic fertilizers such as manure of animals or birds, are the best means for plant nutrition and the increase of soil fertility. Essential nutrients necessary for plants are well-balanced in such fertilizers. When using one-, two- or three-component fertilizers, especially in large

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Peer review under responsibility of Journal Annals of Agrarian Science.
http://dx.doi.org/10.1016/j.aasci.2016.05.013

amounts, it is possible that some nutrients are blocked by others or plants are excessively fertilized. For example, increased amount of nitrogen blocks imbibition of phosphorus. Large amounts of synthetic mineral fertilizers contaminate the environment, they are washed out and get into the ground water; they even reduce the amount of humus in the soil and accordingly reduce soil fertility.

Recently, natural zeolites of sedimentary origin are widely used in practice of plant growing both as substrate components for green houses and the basic material to prepare fertilizers (substitutes for mineral fertilizers) for application under field conditions [2]. The latter allows to reduce doses of mineral fertilizer accepted for plant growing and in some cases makes it possible not to use it. As a result of such measures, environmental hazard diminishes and therefore it is possible to harvest ecologically safe agricultural products.

The results of studies of the effect of zeolites on productivity of green vegetables show that the addition of clinoptilolite-containing tuffs to the content of ionite substrates increases the total productivity of five lettuce cultures grown in those substrates. It should be noted that the productivity of a biomass increases almost twice in the substrate containing 90% of clinoptilolite in comparison with the control [3].

In [4], fulfilled in Italy, it was shown that adding the yellow tuffs into the soil composed of 37% phillipsite and 17% faujasite in amount of 100–300 g/m^2 promotes the increase of germinating ability of spinach seeds by 39.2% and the crop yield by 21.2% in comparison with control (at the content of tuff in the soil of 300 g/m^2). Adding of tuff consisting of 9% phillipsite and 61% chabazite into the soil increases the height of plants up to 29.6% in comparison with control (no fertilizers in the soil).

In [5], fulfilled in Georgia, it was shown that the addition of phillipsite-containing rocks into the soil (village Shukhuti, Georgia; mineral content 60–90%, cation content is mainly represented with potassium) under vegetation conditions significantly increases (by 92.3%) productivity of cress without using mineral fertilizers.

The authors of [6] present the results of the study of the impact of zeolite-containing rocks and rocks with high-content of calcium cations (marl) on yield of grain the crop and green mass of maize. The results indicate that the above-mentioned yield may be increased without mineral fertilizers using zeolite containing rocks and the local raw material – marl. Deposits of this mineral are widely propagated in the region where field works on cultivation of maize were fulfilled.

Analyzing studies of national [7–10] and foreign [11–13] researchers, some viewpoints are determined, which allow to get positive results of the effect of natural zeolites on the growth and development of plants. As a result of applying natural zeolites into the soil, the formation of vegetation and generation of organs of plants go faster, photosynthetic apparatus is developed, which, as a result, leads to the formation of early harvest of crops [14].

Zeolites belong to the group of cation exchangers and their saturation with cations of ammonium, potassium, calcium, magnesium, zinc and others is not difficult. As for phosphorus, it is a part of anionic acid residue in corresponding salts. The influence of phosphorus on plants life is not simple. At the normal nutrition with phosphorus the harvest increases significantly and the quality of grains improves. Content of sugars increases in vegetables, fruits and root crops, the amount of starch increases in potato tubers, the height of lint and strength of fiber grow. Phosphorus improves winter resistance of plants, promotes their development and maturing. Phosphorus is a part of phosphatides forming protein-lipid cellular membranes and regulating their penetrability into different matters. Significant amount of phosphorus in plants exists as a part of phytin, which represents the storage matter in seeds and important element in the process of germination. Phosphorus is also a part of vitamins and many enzymes. It is important in the processes of energy exchange and plant metabolism. Phosphorus participates in the processes of carbohydrate and nitrogen exchange, photosynthesis, breathing and fermentation [15,16].

In the nature, there are no natural sources of replenishment of soil with phosphorus, therefore the only possible way for this is the use of phosphate fertilizers. As early as 1983, the group of researchers [17,18] used two methods for enrichment of natural zeolites with phosphorus, mainly, with clinoptilolite-containing tuff. The substance obtained consisted of citric-soluble calcium phosphate up to 75%.

In [19] the method is supposed to obtain a new anion exchanger on the basis of synthetic zeolites of A, X and Y types. Phosphorus-containing aluminosilicate does not lose structure of zeolite but acquires an anion exchange capacity due to the formation of a new phase.

Objectives and methods

Natural zeolites are nanophorous crystalline hydrated aluminosilicates, tetrahedrons of which compose long chains. The structure of their lattice contains cells occupied by free moving ions and molecules of water. After nanomodification (by the thermal or chemical treatment) it is possible to break long chains of the aluminosilicate structure. Simultaneously, free-migrating ions and molecules of water are isolated from zeolite pores. As a result the structure of zeolite, its porosity, surface volume and dimensions of nanoporous may be changed or new nanoporous may occur [20].

Clinoptilolite enriched with phosphorus was prepared according to the method in [19]. With this aim clinoptilolite-containing tuff from the Dzegvi deposit (Eastern Georgia) with the content of the main mineral within the 75–85% was mixed with ammonium dihydrophosphate in the ratio 1:1 and fused at 250 °C without mixing for 25 h. The product obtained was pink, nonhygroscopic, hard and optically homogenous.

The product obtained in such a way keeps the structure of zeolite and contains exchangeable ions of ammonium, potassium and phosphorus. Cation content of used clinoptilolite contains mainly cations of calcium, sodium and potassium. Intrusion of amorphous mass of salt into the clinoptilolite structure on the nanolevel causes certain deformation of its structure that is clear by changes in the X-ray diffractogram (Table 1).

Table 1 – Reflex intensity (I) and interplanar spacing (d, nm) for the studied clinoptilolite specimens.

Clinoptilolite		Clinoptilolite + $NH_4H_2PO_4$	
I	d	I	d
10	9.54	–	–
		23	8.672
36	7.846	–	–
6	7.357	–	–
–	–	48	5.724
11	5.155	–	–
14	5.073	–	–
18	4.817	–	–
27	4.358	18	4.336
100	3.955	67	3.854
28	3.396	18	3.601
62	3.302	58	3.302
37	3.038	–	–
51	2.242	80	2.954
29	2.779	–	–

In the process of fusion, water desorbs out of the zeolite channels, cations migrate and instead of them the molecules of ammonium dihydrophospate occupy the channels changing the structure of zeolite on the nanolevel, though the main microporous structure of clinoptiloliteis is kept. This is confirmed by X-ray diffraction and IR-spectroscopy studies.

The fact of penetration of salt into the structure of zeolite shows the presence of additional bands on the diffractogram of the fusion specifying dihydrophosphate. Moreover, in the IR-spectra of the fusion additional bands appear as well, which are typical for P=O– and P–O–P bonds in the range of both deformation and stretching vibrations [21,22].

The analysis of the framework vibration segment of IR spectrum of zeolite (400–1400) cm^{-1} (Fig. 1) shows that after fusing zeolite with salt its structure is fully kept. This is also confirmed by the presence of bands typical for symmetric and antisymmetric deformation vibrations at 526, 605, 675 and 1215 cm^{-1}. The basic change in IR spectra is marked for high intensity bands at 1067 and 1215 cm^{-1}, typical for intra- and inter tetrahedron antisymmetric vibrations. The penetration of ammonium dihydrophosphate into the structure of zeolite and appearance of phosphate-ion bond caused the widening of this band and appearance of additional bands about 955 cm^{-1} for vibrations P–O–P bonds; 1145 cm^{-1} for P=O –bond and 575 cm^{-1} for deformation vibrations. As P=O– bond is shorter than Si–O and Al–O– bonds [23], the absorption band of inter tetrahedron antisymmetric stretching vibrations shifts to the higher frequencies from 1067 to 1082 cm^{-1}. The shift of bands of intra- and inter tetrahedron stretching vibrations from 730 to 800 cm^{-1} in the initial form to 780 cm^{-1} in the fused form is provoked by small deformation of the structure of zeolite. Band 1410 cm^{-1} is typical for N–H– bond.

Earlier, this material was used as fertilizer for cultivation of garlic with positive effect [3]. It is known that when applying mineral fertilizers for plant growing it is necessary to apply them into soil every year, and in some cases repeated placement is needed because of washing-out by ground waters.

Our study was conducted to determine the aftereffect of supposed fertilizer in the subsequent years after placing it into soil, in the present case in the next year of the experiment. The test cultures were representatives of lily-family: bulb

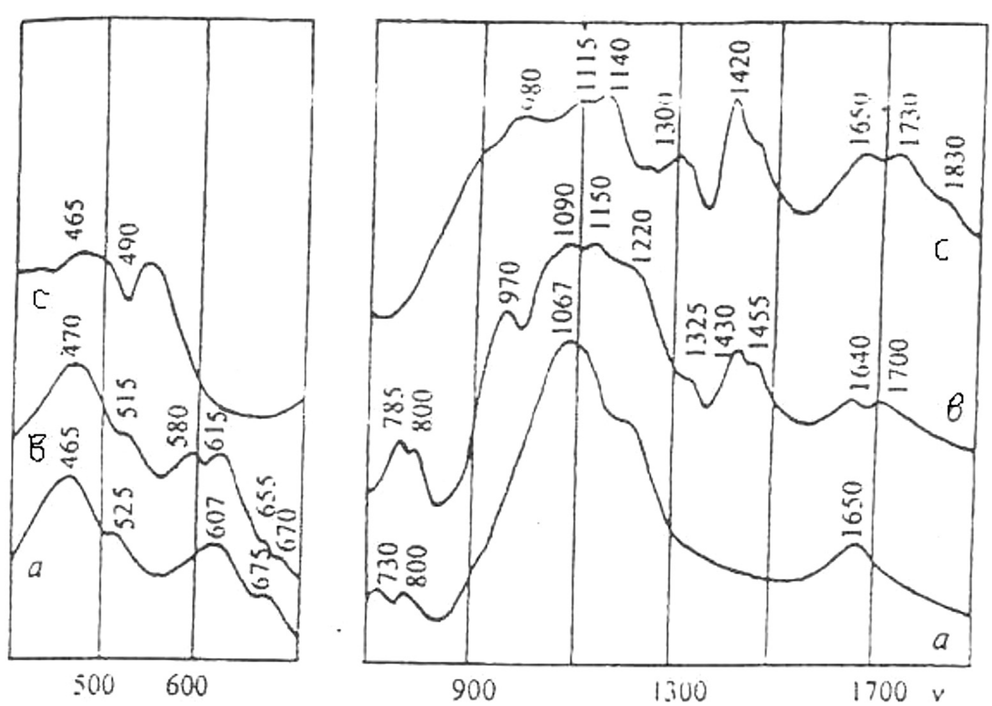

Fig. 1 – IR-spectra in the range of vibration frequencies of aluminosilicate-oxygen frame of a) initialclinoptilolite; b) phosphorus-containing clinoptilolite; c) ammonium dihydrophosphate.

onion (*Allium cepa* L) and garlic (*Allium sitivum* L). Both cultures were sown by bedding sets (daughter bulbs). The experiment was conducted under field conditions on the farm of the village Tsaishi, Zugdidi district, western Georgia. The soil was ash gray with low humus.

Experiments were conducted in six variants with four repetitions for each culture on 10 m^2 plots (48 plots). The first variant – pure soil (control), the second – soil enriched with mineral fertilizers with the contents: $N_{60}P_{80}K_{50}$ kg/ha for onion and $N_{70}P_{80}K_{60}$ kg/ha for garlic. Both variants served as subjects for the comparison. In variants 3–6-only nitrogen-phosphorus-containing clinoptilolites were applied in amount of 10, 15, 20 and 25 t/ha, respectively.

Before sowing onion and garlic, mineral fertilizers (variant 2) and finely-ground ammonium-phosphorus-enriched form of clinoptilolite tuff (variants 3–6) were placed into soil by ploughing manually. These fertilizers were added into plots only in the first year of the experiment (2001). The following year sowing of onion and garlic was realized without using fertilizers (except variant 2), i.e. the experiment aimed to reveal the aftereffect.

In the experiment the following onion cultivars were used: bulb onion, semihot breed "local Vanuri" –zoned for Zugdidi district, weight of sets 1.3–1.4 g, sowing frequency 50 sets per m^2. In two-year experiment just this variety of the onion uses shown.

In 2001 onion sets were sown on 19 March, bulbs were gathered on 4 July, duration of the experiment 146 days. In 2002 sowing of onion was performed on 4 Februaty, gathering – on 7 July, duration of the experiment 151 days.

In the first year of the experiment (2001) garlic breed "local imeruli" was sown, winter variety, nonbolting, with small simple cloves. Sowing was performed on 22nd November, 2000, gathering bulbs – on 29th May 2001, duration of the experiment 189 days. In the second year (2002) for the sowing a breed of garlic "Polyot" was used, bolting, with large cloves (average weight of a clove 4.0–4.1 g). Sowing was performed on 9th December, 2001, gathering bulbs – on 2nd of June, 2002, duration of the experiment 206 days. Allocation of the sowing material – drilled sowing, the distance between holes – 10 cm and between rows – 20 cm.

The aim of the present experiment was to study the effect and aftereffect of nitrogen-phosphorus-containing clinoptilolite placed in the soil on the productivity of bulbous cultures for the period 2001–2002 and on some biometrical indices of bulbs of onion and garlic.

Results and analysis

Table 1 shows averaged results of the productivity of the bulbous cultures obtained by the experiment, i.e. of four repetitions for each variant calculated in dt/ha, also comparative indices of the productivity (CIP) in percent towards the productivity for onion and garlic grown in variants 1 and 2, respectively [3]. All numerical results were treated by mathematical and statistical methods with the determination of the least essential difference ($HCP_{0,5}$) and relative accuracy of the field trial ($S\bar{x}\%$) [24].

Table 2 – Influence of nitrogen-phosphorus-containing clinoptilolite ($ClNH_4^+PO_4^-$) introduced into the soil on some biometric indices of onion and garlic bulbs grown in 2001–2002.

#	Variants	Bulb onion, the species "Local Vanuri"										Garlic, the species "Polyot"				
		2001					2002					2002				
		Average weight of a bulb, g	Length of bulbs, cm	Widthof bulbs, cm	Volume of bulbs, cm^3	Form indices of a bulb	Average weight of a bulb, g	Length of bulbs, cm	Widthof bulbs, cm	Volume of bulbs, cm^3	Form indices of a bulb	Average weight of a bulb, g	Length of bulbs, cm	Widthof bulbs, cm	Volume of bulbs, cm^3	Form indices of a bulb
1	Soil without fertilizers (control)	41.1	2.5	3.5	8.7	1.40	39.5	2.5	3.3	8.4	1.32	32.2	1.7	3.1	5.3	1.82
2	Soil with mineral fertilizers[a]	42.3	2.6	3.6	9.4	1.38	43.6	2.7	3.7	10.0	1.37	35.1	1.9	3.4	6.4	1.78
3	Soil + $ClNH_4^+PO_4^{-3}$-10 t/ha	47.6	3.0	4.0	12.0	1.34	50.4	3.1	4.3	13.2	1.38	43.6	2.3	4.2	9.7	1.82
4	Soil + $ClNH_4^+PO_4^{-3}$-15 t/ha	42.4	2.6	3.6	9.3	1.38	47.8	3.0	4.1	12.2	1.36	46.6	2.5	4.5	11.2	1.80
5	Soil + $ClNH_4^+PO_4^{-3}$-20 t/ha	46.4	2.9	3.9	11.4	1.34	49.7	3.1	4.2	13.1	1.35	42.3	2.2	4.1	9.0	1.86
6	Soil + $ClNH_4^+PO_4^{-3}$-25 t/ha	44.1	2.7	3.7	10.1	1.37	47.7	3.0	4.0	12.1	1.33	39.1	2.1	3.8	7.9	1.80

[a] Mineral fertilizers for bulb onion were used in an amount of $N_{60}P_{80}K_{50}$ kg/ha and for garlic – $N_{70}P_{80}K_{60}$ kg/ha.

Table 3 – Influence of nitrogen-phosphorus-containing clinoptilolite (NH4+PKл) introducing into the soil on the productivity of Bulb onion and garlic, t/ha (average from four replications) in 2001–2002.

#	Variants	Bulb onion, species "Local Vanuri"						Garlic, species "Local Imeruli"			Garlic, species "Polyot"		
		2001			2002			2001			2002		
		Average productivity	CIP % in relation to variant 1	CIP % in relation to variant 2	Average productivity	CIP % in relation to variant 1	CIP % in relation to variant 2	Average productivity	CIP % in relation to variant 1	CIP % in relation to variant 2	Average productivity	CIP % in relation to variant 1	CIP % in relation to variant 2
1	Soil without fertilizers (control)	205.4	–	6.5	197.9	–	−9.1	65.0	–	12.2	160.1	–	−8.0
2	Soil with mineral fertilizers[a]	192.8	−6.1	–	217.8	10.1	–	74.0	13.8	–	175.8	9.8	–
3	Soil + $ClNH_4^+PO_4^{-3}$-10 t/ha	205.5	9.3	16.9	252.8	27.7	16.1	78.0	20.0	5.4	217.9	36.1	23.9
4	Soil + $ClNH_4^+PO_4^{-3}$-15 t/ha	224.4	9.3	16.4	239.4	21.0	9.96	76.0	16.9	2.7	232.9	45.5	32.5
5	Soil + $ClNH_4^+PO_4^{-3}$-20 t/ha	229.8	11.9	19.2	248.1	25.7	14.2	83.0	27.7	12.2	229.5	43.3	30.5
6	Soil + $ClNH_4^+PO_4^{-3}$-25 t/ha	220.6	7.4	14.6	245.4	24.6	12.8	80.3	23.5	8.5	195.4	22.1	11.2
		$HCP_{0.5}$ = 9.2 dt/ha; $S\bar{x}\%$ = 1.4			$HCP_{0.5}$ = 10.6 dt/ha; $S\bar{x}\%$ = 1.6			$HCP_{0.5}$ = 4.9 dt/ha; $S\bar{x}\%$ = 0.85			$HCP_{0.5}$ = 6.3 dt/ha; $S\bar{x}\%$ = 1.1		

[a] Mineral fertilizers for bulb onion were used in the amount of $N_{60}P_{80}K_{50}$ kg/ha and for garlic – $N_{70}P_{80}K_{60}$ kg/ha.

From the data analysis, given in Table 1, it is clear that the productivities of both cultures accords an average productivities of these cultures grown on the territory of the country and in the case of garlic even somewhat exceeds it [25]. Significant difference in the productivity according to years (2001 and 2002) is caused by that in 2002 another breed was sown with typical large cloves giving the higher yield than small cloves [24]. It should be noted that in the second year of trial, in difference with the first year, the effect of ordinary mineral fertilizers on the yield of garlic became less. The influence of nitrogen-phosphorus-containing clinoptilolite on the garlic productivity in the second year of the experiment somewhat increased in comparison of the first year. Thus, the highest yield of garlic in 2001 was fixed when modified clinoptilolite in amount of 2 kg/m^2 (calculating as 20 t/ha) was introduced in the soil. The effect was higher by 12% than the effect of mineral fertilizers. In the second year the effect increased up to 31%. In the case of onion the highest yield of this crop in the first year was reached at applying the supposed fertilizer in amount of 2 kg/m^2. The effect was higher by 19% than in case of the mineral fertilizer, in the second year it was higher only by 14%.

Thus, the application of nitrogen-phosphorus-containing clinoptilolite in the soil in amount of 1–2 kg/m^2 is more effective than that of mineral fertilizers, and, in addition, has a well revealed aftereffect.

As follows from the data of Table 1, the garlic culture is more sensitive to the positive effect of nitrogen-phosphorus-containing clinoptilolite than onion. This is tentative assumption only, which requires further verification by the implementation of large-scale field trials. In Table 2 some biometric indices of onion and garlic bulbs are given: average weight, length, width, volume of the bulb and their forms' index in dependence of nitrogen-phosphorus-containing clinoptilolite effect.

One can observe certain correlation between data in Tables 2 and 3, mainly, the largest in the mass and volume bulbs of onion and garlic are grown at placing of such amount of the fertilizer into the soil, which promotes the highest yield of that cultures. In the case this is 1.5–2 kg/m^2 of nitrogen-phosphorus-containing clinoptilolite. It is noticed that such an impact is more revealed in garlic that in onion (in the sense of the improvement of the biometric indices). In this point of view nitrogen-phosphorus-containing clinoptilolite, in comparison with mineral fertilizers, promotes the increase of the average weight and mass of garlic bulbs by 25–30% in average, and that of onion by 12–13% only.

Conclusion

Thus, the preliminary obtained data give evidence of applicability of fertilizers prepared on the basis of clinoptilolite enriched by ammonium and phosphorus ions for growth of such crops as bulb onion and garlic. The fertilizer is the match for farms producing ecologically safe production.

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