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Nitrogenous zeolite nanomaterial and the possibility of its application in agriculture

G. Tsintskaladze [a], L. Eprikashvili [a, *], N. Mumladze [b], V. Gabunia [a], T. Sharashenidze [a], M. Zautashvili [a], T. Kordzakhia [a], T. Shatakishvili [a]

[a] *Ivane Javakhishvili Tbilisi State University, Petre Melikishvili Institute of Physical and Organic Chemistry, 31, Politkovskaya Str., Tbilisi, 0186, Georgia*
[b] *Cartlis Agrosystems Ltd, 75[b], Kostava Str., Tbilisi, 0160, Georgia*

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ABSTRACT

New nanotechnological method is proposed to reduce the negative effects of nitrogenous fertilizers and their losses, which involves introduction of nitrogen-containing substance into the structure of natural zeolite. The obtained nanomaterials can be used as a nitrogen fertilizer, which allows the gradual transfer of nitrates into the soil and minimizing fertilization losses. It also significantly reduces groundwater contamination. Also, volatilization as well as drain losses of nitrogen are significantly reduced. Proposed zeolite nanomaterial represents a strong reserve of nitrogen compounds required for feeding the plants. Obtained nanomaterial structure is studied using chemical, X-ray diffractometric and IR spectroscopic methods. Also, nanotechnological process of enrichment and extraction of natural zeolite with ammonium nitrate is established. For proving the effectiveness of proposed nitrogenous fertilizer tests were conducted on corn crop (108 m^2) where the average harvest on the recording area amounted 92.6 kg. In addition to the field test, the production test was also conducted on 1 ha where the increased corn crop reached 1.4 t/ha which is equal to 18.9%.

Introduction

Providing the population with environmentally friendly products is one of the greatest challenges of our time. Nowadays, it is impossible to get a high harvest without using mineral fertilizers in agriculture. Although, using increased amount of these fertilizers can negatively affect the quality of nutrients as well as the biochemical area of the environment.

Soil and vegetation is a united, interconnected system. One of the most important features of the soil is the ability to satisfy plant's requirements for food and water. Soil is a source of macro- and microelements required for the plant, which can be absorbed by its roots system and its leaves [1,2].

Today, out of all mineral nitrogen fertilizers, ammonium nitrate is most widely used in the world. The plant needs big amount of ammonium nitrate for growing its green mass and providing high crop. Nitrogen is the main nutrient that produces organic substances for the plant. Except for amino acids, nitrogen is also included in purines, alkaloids, enzymes, plant growth regulators, chlorophyll and cellular membranes. Nitrogen deficiency leads to the failure of the synthesis of normal amount of chlorophyll and eventually the leaves of the plant are diseased with chlorosis. Nitrogen circulation in the plant is especially intensively observed at the maximum index of its height. Plants are mainly using ammonia and nitrous nitrogen, while legumes and some other plants are using molecular nitrogen in Symbiosis with microorganisms [3–5]. Ammonium nitrate contains nitrogen both in nitrous and ammonia forms. Therefore, while using this fertilizer nitrogen volatilization as well as nitrogen losses from drained soil occurs. Nitrous nitrogen drained in the soil is heavily polluting groundwater [6]. The problem of the loss of nitrous and ammonia nitrogen and the threat of environmental hazard in the world has not been solved yet due to the fact that ways of retention of nitrous nitrogen in the soil is not found so far. Because of that, the farmer has to introduce ammonium nitrate into the soil minimum of 2–3 times during the life cycle of the plant, which is associated with additional problems. Therefore, it's becoming more and more common to use non-traditional mineral-raw resources like diatomite, marlstone, limestone, zeolites, tuffs and other materials in farming [7,8].

* Corresponding author.
E-mail address: leprikashvili@hotmail.com (L. Eprikashvili).
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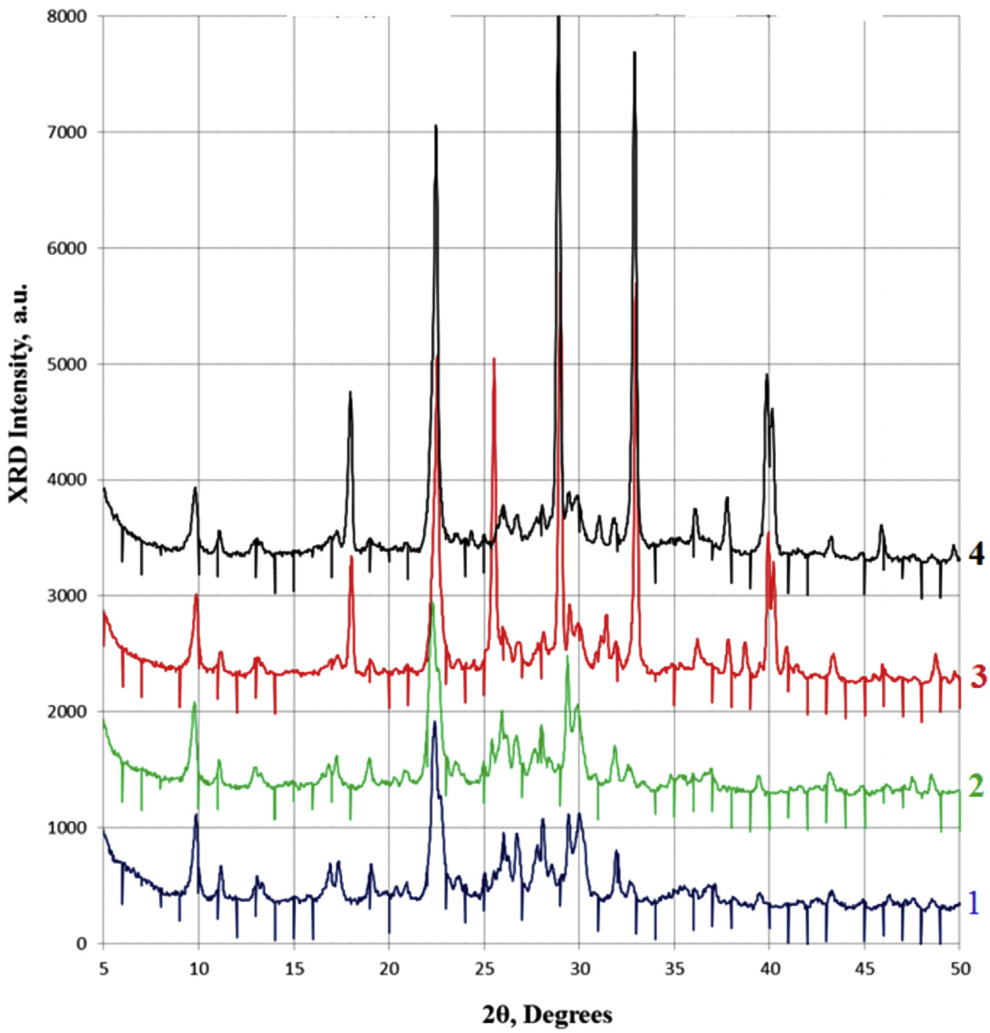

Fig. 1. *X-Ray diffractograms of zeolite clinoptilolite:*
1. Natural zeolite (clinoptilolite);
2. The zeolite material after complete leaching of nitrate ions.
3. The zeolite material after complete leaching of nitrate ions (1:1).
4. The zeolite material after complete leaching of nitrate ions (1:3).

Natural zeolites represent crystalline-hydrating aluminosilicates the structure of which contains gaps that are occupied by ions able to move freely and water molecules. Zeolites are nanoporous materials whose thermal or chemical processing can result in breaking of zeolite structure chains that may be followed by some changes in its structure. By leaving the zeolite structure by ions and water molecules and changing the internal volume it is possible to change the sizes of nanopores as well as creating new nanopores [9].

Georgia is rich in different types of zeolite-contained tuffs. There are 15 varieties of zeolite minerals researched in Georgia, the supply of which is approximately 300 million tons [10].

The use of natural zeolites turned out to be especially effective in agriculture [11,12]. The introduction of mineral fertilizers along with natural zeolites containing environmentally safe microelements into the soil allows us to ensure the duration of the effect of the introduced fertilizer and to reduce the drain of nutrient components. In addition, zeolites regulate the process of water, nitrogen, potassium and other macro and microelements absorption by the plant into the soil [13]. Nowadays, zeolite fertilizers are widely used in the practice of plants as part of substrates used in greenhouse farms as well as fertilizer basis used in open grounds [14].

Objectives and methods

As it was pointed out, natural zeolites have a developed and organized micro- and nanoporous crystalline structure. Unlike synthetic zeolites additionally they have secondary, so called mesoporous structure as well. If we add main adsorption and molecular-sieve features of natural zeolites to it, in order to limit nitrogenous fertilizer's negative movements according to all above mentioned and also, to significantly increase the nitrogen absorption coefficient of the plant, we have proposed a new, nanotechnological method [15,16] which allows us to introduce nitrogenous fertilizer, namely ammonium nitrate in a way that zeolite structure won't be violated. Obtained nanomaterial – “inorganic capsule molecular sieve” can be used as nitrogenous fertilizer which allows us to regulate the gradual transition of nitrates into soil, minimize the waste of fertilizer, and also significantly reduce the pollution of ground waters by nitrates.

Natural zeolite found in Georgia (Kaspi region, upper Khandaki)

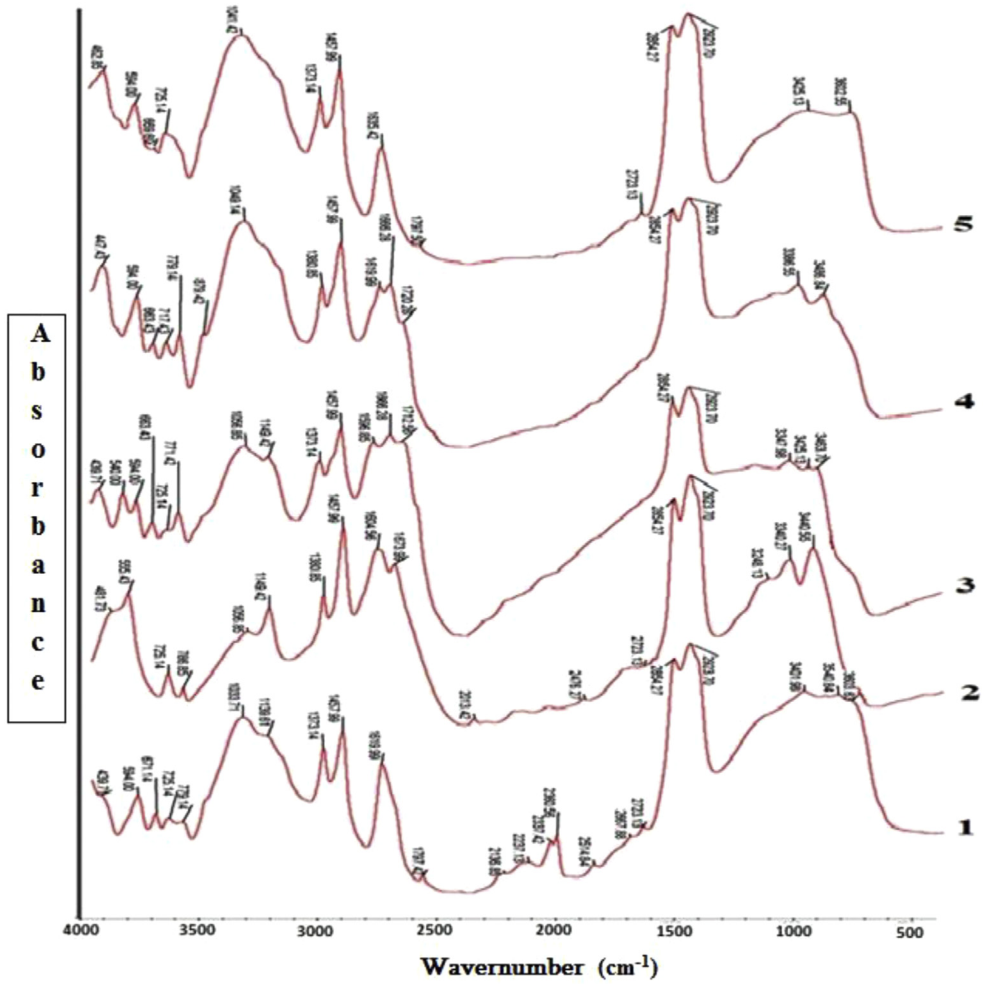

Fig. 2. *IR spectra of the samples:*
1. Natural zeolite (clinoptilolite);
2. Salt - ammonium nitrate;
3. The zeolite material is enriched with ammonium nitrate;
4. The zeolite material partial leaching of nitrate ions;
5. The zeolite material after complete leaching of nitrate ions.

- 0.5 mm clinoptilolite and ammonium nitrate was used for the experiment. The materials have been mixed in different proportions and then saturated with molten salt for an amount of time. Produced nanomaterial, which is characterized by optical homogeneity and mechanical stiffness, was cooled down to room temperature and then grinded and granulated to grains sized 0.5–2 mm.

The structure and features of nanomaterial, enriched with new zeolite nitrates was examined with chemical, X-ray diffractometric and spectroscopic methods. It was concluded that after the introduction of ammonium nitrate into zeolite pores, the structure of zeolite did not change, also the nanotechnological gradual extraction mechanism of ammonium nitrate from zeolite structure was established.

Fig. 1 shows X-ray diffractograms of zeolite clynoptilolite: initial zeolite (1); samples fused with ammonium nitrate with ratios 1:1 (2) and 1:3 (3); zeolite after being fully flushed with ammonium nitrate water (4) (Fig. 1).

As it is shown on X-ray diffractograms, after enrichment with ammonium nitrate, the structure of zeolite remains practically the same, except for some minor deformations of the structure, which are identified by X-ray diffractogram differences between peaks intensities, which is typical for clinoptilolite. 2nd and 3rd diffractograms clearly illustrate unchanged structures of salt, as well as zeolite that was our goal. Nanotechnological process of enrichment and extraction of natural zeolite with ammonium nitrate studied with IR spectroscopy method is shown on Fig. 2 (Fig. 2).

As we can see from the diagram, zeolite as well as ammonium nitrate IR spectrums dramatically differ from each other and they both correspond to the etalon spectrums which are characteristics of each of these substances [17]. Zeolite IR spectrum has significantly changed after it was nanotechnologically treated with ammonium nitrate and the result as it was expected is significantly different from the initial IR spectrums of both clinoptilolite and ammonium nitrate. As we can see from the diagram, there are noticeable changes in the structure of zeolite which is expressed in IR spectrum in forming new lines and also in changes of the frequency and intensity of the existing lines. In particular, in the deformation and valency vibration regions of aluminosilicate we have new lines - 594, 1596, 1712; also, lever - 879 cm^{-1}, which are characteristics to nitrate ions [18]. Frequencies of the deformation and valency vibrations of the lines of aluminosilicate have changed from 1033 cm^{-1} to 1056 cm^{-1}, from 1139 cm^{-1} to 1149 cm^{-1}, from 3401 cm^{-1} to 3347 cm^{-1}, from 3540 cm^{-1} to 3425 cm^{-1} and from

Table 1
Corn hybrid PR32F73 grain crops in the field test in the research area.

Scheme of the test	Corn grain crop - 94,5m^2 (kg)				Average corn crop	
	I Repetition	II Repetition	III Repetition	IV Repetition	Kg in repetition	tone/ha
Version I	73,1	78,1	73,0	75,8	75,0	7,9
Version II	84,8	83,4	86,5	85,6	85,0	9,0
Version III	85,2	83,0	86,1	82,2	84,1	8,9
Version IV	91,0	90,5	95,3	93,6	92,6	9,8

Table 2
Corn hybrid PR32F73 grain crops in the production test in the research area.

Version	Corn grain crop t/ha	increase in crop	
		t/ha	%
300 kg/ha ammonium nitrate	7,4		
75 kg/ha zeolite +225 kg/ha nitrate	8,8	1,4	18,9

3603 cm^{-1} to 3463 cm^{-1}.

After treating some amount of resulted nanomaterial with water, the intensity of lines typical to nitrate ions in IR spectrum is reduced. Also, the frequencies and intensities between the lines, which we had in initial and nanomodified examples of zeolite are reduced. After full water flushing of ammonium nitrate ions from the zeolite structure the IR spectrum is almost equal to the initial IR spectrum of zeolite. The difference is only changing the frequency and intensity of some lines which is resulted by partial deformation of zeolite structure. This fact once again proves that ammonium nitrate has entered the zeolite structure. Thus, the results obtained by X-ray diffractometer analysis as well as the results of IR spectroscopic method are equal.

As pointed out, after the introduction of nitrogenous fertilizer, in particular, ammonium nitrate into the soil, due to the big consumption of nitrate and ammonium fertilizers, introducing them into the soil must be repeated several times in some cases. The ions of ammonium nitrate from proposed nanomaterial are slowly allocating into the soil from its porous structure and is slowly transmitting to the plant due to molecular-sieve characteristics of zeolite, so that the loss of nitrogen is minimized and nitrogen transferred to soil is used completely during whole life cycle of plant.

Results and analysis

Proposed nitrogenous fertilizer was tested for its effectiveness on corn crop, in particular on PR32F73. Four options of a field test were conducted with the following scheme:

1. Ammonium nitrate with physical weight - 300 kg/ha (102 kg/ha pure nitrogen);
2. Zeolite with physical weight - 300 kg/ha + ammonium nitrate with physical weight - 300 kg/ha (102 kg/ha pure nitrogen);
3. Zeolite with physical weight - 200 kg/ha + ammonium nitrate with physical weight - 200 kg/ha (68 kg/ha pure nitrogen);
4. Zeolite with physical weight - 75 kg/ha + ammonium nitrate with physical weight - 225 kg/ha (76.5 kg/ha pure nitrogen).

The field test was set on 108 m^2. The recording area - 94.5 m^2; the distance between the rows - 75 cm; the distance between the plants in a row - 18 cm. The best crop of corn grain was observed in the 4th version where the harvest on the recording area reached an average of 92.6 kg. In the case of introducing nitrogen fertilizer alone the average harvest on the recording area was 75 kg. There was no credible growth noticed in the crop between 2nd and 3rd versions (Table 1).

Production test was conducted along with the field test on the above mentioned version. Division space - 1 ha. Test scheme is the following:

1. 300 kg/ha ammonium nitrate (with physical weight);
2. 75 kg/ha zeolite +225 kg/ha ammonium nitrate (with physical weight).

In the first version the corn grain crop amounted 7.4 t/ha and in the second version it amounted 8.8 t/ha of corn grains. The increase amounted 1.4 t/ha which is equal to 18.9% (Table 2).

Conclusion

Thus, the zeolite nanomaterial obtained by the proposed method can successfully be used as a prolonged action nitrogenous fertilizer to provide a plant with nitrogen throughout the whole vegetative period. The introduction of this fertilizer into the soil is done only once which reduces logistic costs, environmentally safe (reduces the flow of nitrates into groundwaters), has a prolonged action. Also, it regulates the absorption of the water and nitrogen by the plant. The above mentioned fertilizer can be used in open field as well as in greenhouse farms, nursery gardens and for decorative home plants.

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