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Nitrate-Free Nutrient Substrate for Plants on the Basis of Clinoptilolite

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Abstract

A recipe for the nutrient granular substrate for growing plants (the working name is "Zion") has been developed. The substrate contains all necessary for plant nutrient elements in the chemically bound state in high concentration; it does not contain any organic matter and nitrates, and does not need additional fertilization during the plant vegetation. All nitrogen in the substrate is contained in ammonium form. The substrate has been tested in the laboratory conditions in pot experiments for fertility and nitrates concentration in thebiomass of the two cultures accumulating a large amount of nitrates that is leaf salad (*Lactuca sativa* l.) cultivar Afficion and ryegrass (*Lolium perenne* l.).The plants were grown on a 100% substrate as well as on its mixtures (3 - 10%) with different fruitless media - quartz sand, peat, and vermiculite. It appeared that in all the cases, when Zion has been used, the maximal content of nitrates in the plant biomass was 209 mg/kg dry, the minimal one was less than 50 mg/kg dry, which is lower by an order of magnitude than the admitted sanitary norm for the plants used in the study.

Keywords: *Nutrient Substrate for Plants; Nitrates; Clinoptilolite; Salad; Ryegrass*

Introduction

All known nutrient media for plants, including natural soils, nutrient soils and hydroponic solutions, contain nitrates as the main source of nitrogen nutrition. Nitrates can accumulate in plants, reaching levels that are hazardous to human health. Despite the fact that their content in plant products can be somewhat reduced by changing the ratio of biogenic ions in the nutrient medium and growing conditions of plants, there is no reliable and practically acceptable way to control their content.

In this communication, we present the formulation of a full-fledged nitrate-free substrate based on the natural mineral clinoptilolite from the zeolite group1 and demonstrated its applicability for obtaining high yields of low-nitrate biomass of two plants, which accumulate a particularly large amount of nitrates in the biomass, when cultivated on natural soils or on hydroponic solutions. Leaf lettuce (*Lactuca sativa* l.) of Afition variety and forage cereal Perennial ryegrass (*Lolium perenne* l.) Were selected as examples. The maximum permissible concentration of nitrates in the raw biomass of these crops is 2000 and 500 mg/kg, respectively [1].

The substrate has the conditional name "Zion" - Zeolite Ion-exchange (Z-ion). It consists of irregular hydrophilic particles with a size of 1 - 3 mm and a bulk density of 1.1 kg/dm^3. Its maximum water absorption is 0.1g of water per gram dry. Contains all nutrients necessary for plants in a chemically bound form. All nitrogen is contained in the form of an ammonium ion; there is no nitrate in the substrate. The ratio of ions in the substrate and the pH of the solution in equilibrium with it can be arbitrarily changed in accordance with the requirements of the user. The composition of mobile ions of one of the substrate variants, which was used for growing plants, is presented in table 1. The concentration of cations in the substrate was determined by the complete displacement of all ions from the substrate with 0.3M HCl, followed by analysis of the extract by capillary electrophoresis (Kapel 104-T device). Phosphates were determined in accordance with the recommendations in [1]. Concentrations in aqueous extracts were obtained as a result of contact of 10g of substrate with 45 ml of water in equilibrium solutions.

Parameter	NH_4^+	k^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}
Content in the substrate, meq / 100 g	37	25	12	1,8	29				7,6*
Content in the substrate, mg / 100 g	666	975	276	21,6	580				722
Conc. in the hood dist. water, meq / l	4,92	1,50	3,33	0,31	0,83	0,85	0,16	0	5,98**
Conc. in the extractor hood water, meq / l	5,35	1,62	3,97	0,48	1,06	1,59	0,65	0,10	4,73**
Conc. in the water. water, meq / l	0	0	0,50	1,34	3,19	0,76	0,54	0,18	0

Table 1: *The content of mobile ions in the Zion substrate pH 7.0 and their concentration in aqueous extracts.*

*Notes: * - Concentration in mmol/100g, ** - Concentration in mmol/l.*

From the data table. Figures 1 and 2 show that the Zion substrate contains all the macroelements necessary for the plant in much higher concentrations than in the soil and other nutrient media used in practice. It does not indicate the content of trace elements, since they are introduced into the substrate in the form of dry salts in accordance with generally accepted recommendations [2] and the needs of crops grown on the substrate and/or the technology of their cultivation. In addition, natural clinoptilolite contains a significant amount of trace elements, which in many cases makes their additional application unnecessary.

At the same time, upon contact with water, it forms a nutrient solution with a concentration and ratio of ions close to optimal [3], which excludes the possibility of an overdose of fertilizers in the substrate solution and allows direct contact of substrate particles with the plant root.

The fact that all nitrogen in the Zion substrate is part of the ammonium ion can be considered as a factor facilitating its assimilation by the plant, since it is directly involved in the synthesis of amino acids, which precedes the formation of proteins [4]. Nitrates absorbed by the plant from nitrate fertilizers do not directly participate in this process. They must be reduced to ammonium ion, which is energy intensive. By using ammonium as the nitrogen source, this multi-stage process is eliminated. The use of nitrates as nitrogen fertilizers is not related to the physiological need of plants and is due to the availability and relative stability of nitrates in soils in comparison with ammonium, which is rapidly oxidized due to microbiological and enzymatic processes. From an agrochemical point of view, nitrification (transformation NH^+ in No^-) occurring in soils is undesirable, since it leads to nitrogen losses for due to the washing out of its products from the soil and their pollution of natural waters, as well as denitrification with the formation of gaseous nitrogen compounds.

Ammonium fertilizers do not have these disadvantages, but they cause soil acidification and require additional application of calcium and/or magnesium carbonates. This, in turn, can suppress potassium uptake. This chain of processes is difficult to control, which is one of the reasons why, in practice, preference is given to nitrate fertilizers [5]. However, the acidification of the nutrient medium of plants, in which the ammonium ion enters in an ion-exchange form, does not occur. It is believed that the reason for the decrease in pH is the absorption of the ammonium ion by the root system of the plant from the neutral salt used as fertilizer.

For example $(NH_4)_2SO_4$) with the release of the anion forming the free acid. In our case, this does not happen, since the role of the anion is played by the crystal lattice of clinoptilolite, which has an uncompensated negative charge. Ammonium ion is absorbed by the root plants only in exchange for the ion of the root metabolite, among which hydrogen ions prevail. The latter cannot leave the clinoptilolite particle, and the pH of the substrate solution remains practically constant. Some shift in pH can occur due to hydrolysis of the formed H^+ -form of clinoptilolite, however, the buffer capacity of the substrate is high and, as it turned out, allows maintaining its acidity at a physiologically acceptable level until almost complete depletion. Below are the experimental data on the cultivation of leaf lettuce (*Lactuca sativa* l.) of the Afizion variety and the forage cereal of the perennial ryegrass (*Lolium perenne* l.).

The substrate Zion and its mixtures with the following practically sterile media were tested as a nutrient medium for plants: 1) quartz sand treated with 2M hydrochloric acid to remove carbonates, oxides and metal hydroxides; 2) practically sterile deoxidized high-moor peat; 3) vermiculite. These media have been tested for leachability. ions produced by water. In all cases, nitrates in the components of nutrient media for plants were absent in measured concentrations. The experimental conditions for growing plants are given below.

Black plastic vases with a height of 8.0 cm and an area of 49 cm^2 (7 × 7 cm) with a volume of 250 cm^3 were filled with 220 cm^3 of a nutrient medium. 36 germinated ryegrass seeds were planted in them according to a stencil; 6 lettuce seeds, of which one plant was left on the 7th day. The duration of cultivation was 30 days, after which the plants were cut at a height of 4 cm and the wet and dry (drying at 90°C) biomass of their aboveground part was determined. Lighting - LED lamps DNBO1-4x9-001 U4.1 "Svetodar" with a ratio of radiation intensity in the red and blue areas 4: 1; photoperiod 18 hours (6.00 - 24.00). The total illumination was 10,000 lx. The temperature was maintained at the level of 20 - 22°C. Threefold repetition. Watering with tap water (composition in table 2). The content of nitrates in raw biomass was determined potentiometrically using a nitrate-selective electrode. The results of these experiments are presented in table 3 and 4.

Nutrient medium	N		k_2O		P_2O_5	
	mg/dm^3	mg/kg	mg/dm^3	mg/kg	mg/dm^3	mg/kg
Zion	5698	5180	12925	11750	6560	5964
Nutrient solution [3]	238	238	710	710	400	400
Chernozem [4]					700	500
Florabel nutritious peat soil *	241	1000	289	1200	241	1000

Table 2: *Comparison of the content of the main nutrients elements for plants in the different nutrient media.*
*Note: * - production of the Republic of Belarus, LLC "Florabel", TU Vy100348359.007–2013.*

Volume percent of Zion	Raw biomass, g / flowerpot		No_3^-, mg/kg of raw biomass	
	I vegetation	II vegetation	I vegetation	II vegetation
3	5,02	2,18	189	25
5	7,79	7,11	29	25
10	7,04	8,39	40	40

Table 3: *Influence of the concentration of Z-ion substrate with a quartz sand mixture on the plant biomass of ryegrass in two consecutive vegetations.*

Composition of the nutrient medium	Biomass, raw, g / pot		No_3^-, mg/kg of raw biomass	
	Salad	Ryegrass	Salad	Ryegrass
1.Zion 10% + sand 90%	3,03	8,02	51	50
2. Zion 10% + sand 60% + 30% vermiculite	4,19	10,06	52	36
3. Zion 10% + sand 60% + 30% vermiculite *	3,61	–	25	–
4. Peat 100%	0,33	0,85	209	44
5. Zion 10% + peat 90%	7,06	10,63	64	39
6. Zion 10% + peat 60% + 30% vermiculite	12,71	10,42	48	70

Table 4: *The mass of the leaves and the content of nitrates in it, which were grown on the mixtures of 10% Z-ion with the various inert media.*
*Note. * - the substrate was treated with a ground extract.*
*Note. * - the substrate was treated with a commercially peat-substrate extract.*

The effect on the yield of lettuce and the content of nitrates in it, the pH value, the N: k ratio and the amount of Zion in a mixture with sterile sand was found out in an experiment with pots with a volume of 50 cm^3. A fourfold repetition, the rest of the experimental conditions were the same as described above.

It is known that the accumulation of nitrates in the biomass of plants strongly depends not only on the species, but also on the growing conditions: the intensity and spectral composition of light, the irrigation regime and water-retaining properties of the soil, the availability of root nutrition, temperature, and other factors. Some of them were studied in the present work and can be summarized as follows.

In all cases, the content of nitrates in plant biomass was 10 - 20 times lower than their maximum sanitary standard for human and animal consumption.

There was no significant difference in the concentration of nitrates in lettuce and ryegrass plants grown under the same conditions (Table 4).

When growing lettuce and ryegrass on mixtures of sand with 5 and 10% Zion, almost the same amount of aboveground biomass was obtained (Table 3 and 5). The plants did not suffer from nutrient deficiencies in the leaner mixture. This means that in a mixture with 10% Zion, a large supply of them remained unused. This is confirmed by the fact that the biomass of ryegrass plants obtained in the second growing season is practically the same as in the first for a 5% mixture and noticeably higher for a 10% mixture. For a medium with 3% Zion, a decrease in yield in the second growing season is obvious, which is caused by its depletion. A higher yield of the mass in the second growing season than in the first one at a 10% mixture is due to the fact that the plants grew on a well-developed root system in the first growing season.

The data on growing lettuce in pots of very different sizes (50 and 250 cm^3) are consistent with this conclusion (Table 4 and 5). The plant biomasses were found to be almost the same.

Lettuce plants grew significantly better on mixtures of Zion with sterile peat than with sand, despite the fact that the supply of root nutrition was the same in both cases (Table 5). The control experiment showed that the yield of lettuce on pure peat was negligible. We considered the possibility that some substances that accelerate plant growth can be extracted from peat with irrigation water. To check this, lettuce growing on a mixture of Zion and sand was watered with water infused overnight on peat (Table 4, lines 2 and 3). Watering with the extract did not improve plant growth. Therefore, we believe that the significantly better growth of lettuce plants on mixtures with peat and vermiculite is caused by better air-water properties of this nutrient medium than that of a sand mixture. Replacing sand with peat and vermiculite did not lead to an increase in the nitrate content in plant biomass. Ryegrass plants were found to be less sensitive to replacing sand with peat.

pH	N : k = 2		N : k = 3		N : k = 4		N : k = 6	
	Mass of plants	No_3^-, mg/kg	Mass of plants	No_3^-, mg/kg	Mass of plants	No_3^-, mg/kg	Mass of plants	No_3^-, mg/kg
5% by volume Zion								
7	3,98	130	4,66	209	–	–	–	–
6	3,53	180	4,82	100	–	–	–	–
10% by volume Zion								
7	4,42	–	4,07	–	4,09	110	4,69	140
5	3,03	100	3,79	180	–	–	–	–
100% Zion								
7	7,89	70	8,52	90	–	–	–	–
6	5,21	70	4,30	120	–	–	–	–

Table 5: *The influence of pH, ratio of N: K and content of Z-ion in a mixture with quartz sand on the biomass production and nitrate content in the salad plant.*

A change in the substrate pH within the range of 5 - 7 and the N: k ratio within the range of 2 - 6 had practically no effect on the nitrate content in lettuce plants, which did not exceed 209 mg/kg (Table 5). Despite the fact that nitrate ions were absent in nutrient media, their small amount is found in plant biomass in all cases. This may be due to the fact that our experiments on growing plants were carried out in non-sterile conditions and in the root zone colonies of nitrifying bacteria could develop, converting part of free ammonium ions into nitrates. It is known that the presence of zeolites and some other mineral sorbents in aqueous media and soils contributes to the development of nitrifying bacteria [6].

Conclusion

The literature also discusses the possibility of synthesizing a certain amount of nitrates by plants by as yet unknown mechanisms [6]. In any case, the content of nitrates grown using 100% Zion substrate or its combinations with infertile soils is many times lower than on conventional nutrient media used in practice for growing green crops. For example, the content of nitrates in seven samples of Afitsion lettuce (living plants in plastic pots with peat mixture) grown in a large agricultural complex and bought in several supermarkets in Minsk turned out to be on average 1474 mg/kg, which corresponds to the official sanitary standard. When using mixtures of the Zion substrate, the maximum nitrate content was 209 mg/kg, the minimum - less than 50 mg/kg. The results of this work show that the use of Zion substrates opens up the possibility of obtaining low-nitrate plant products that meet significantly higher sanitary requirements than currently accepted ones.

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