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Original article

Effects of mechanically activated clinoptilolite zeolite on growth of perennial leguminous grasses

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ABSTRACT The results of research on the influence of clinoptilolite zeolite, phosphorus-zeolite, and zeolite-organic fertilizers on seed germination and growth of perennial legume grasses by laboratory phytotesting in grey forest soil are presented. It was found that as a result of filling the interpolymer complex with clinoptilolite zeolite, hydrogen bonds are formed between carbonyl groups of polyacrylamide and silanol groups of the mineral. The important role of the size factor in the influence of fertilizer on plant growth has been established. It is shown that mechanically activated clinoptilolite-rich rock (mechanical energy dose 2.4 kJ·g^{-1}) and the polyvinyl alcohol/polyacrylamide interpolymer complex resulting from mixing equivolume aqueous solutions with concentrations of 4 g·dL^{-1}, filled with 0.4 wt % mechanically activated clinoptilolite-rich rock (mechanical energy dose 3.8 kJ·g^{-1}), have a positive effect on germination and stem length of perennial legume grasses of meadow clover, eastern galega, and sand sainfoin in dark grey forest soil.

KEYWORDS clinoptilolite zeolite, mechanochemical activation, PVA/PAA interpolymer complex, phytotoxicity index, perennial legume grasses

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1. Introduction

Sustainable agriculture is inseparable from the use of environmentally pure materials, including zeolites [1,2]. Natural aluminosilicates improve hydraulic conductivity in a saturated state, infiltration rate, cation-exchange capacity, and water-holding capacity of soil [3, 4], compost quality [5], and nutrient availability [6, 7]. The use of clinoptilolite zeolite in agriculture [8–10] is due to its unique properties and framework nanoporous structure [11], and the product containing at least 50 % of zeolite mineral is called '*zeolitite*' [12]. Zeolites provide moisture maintenance in the soil [12–15] and prolonged fertilizer action (prolongation effect) [13].These nanoporous minerals prevent leaching of nutrients [3, 9, 13] and reduce losses of chemically active gaseous nitrogen [16, 17].

Modified zeolites are also used as highly effective fertilizers [14]. For example, the addition of alginate-zeolite iron (3 : 1) to 150 ppm supports the growth of shallot (*Allium cepa L. 'Bima Brebes'*) tubers, number of leaves, and photosynthesis rate [15]. Zeolite in combination with urea significantly increases nutrient retention [18] and rice yield [10], and they increase spring wheat grain yield by 44 % [19]. Soil application of zeolites added to compost in a vineyard effectively mitigates the effects of climate change [20]. Zeolite and calcium-magnesium phosphate fertilizer improve compost quality by effective passivation of Cd (II) [21] and heavy metals [5]. Application of zeolite with potassium dihydrophosphate or zeolite with diammonium hydrophosphate reduces the content of exchangeable Cd in the soil [22]. Clinoptilolite zeolite modified by ammonium chloride contributes to the control of nitrogen release [23]. Ion exchange of zeolite with ammonium increases the moisture holding capacity of substrates, while ion exchange with potassium decreases it [24]. Phosphate ions are sorbed on the clinoptilolite framework and participate in the formation of surface complexes [25,26]. Ammophos fertilizer enriched with clinoptilolite increases the yield of cucumber (*Cucumis sativus*) in dark chestnut soil [27] and also reduces excessive use of chemical fertilizers by 25 % [28, 29]. Organ-zeolite soil systems increase the mass and length of maize cobs [30] and restore vegetation on infertile metal-contaminated soils [5].

Seed germination is affected by the dispersibility of ion exchange clinoptilolite [24]. Nanozeolite with a particle size of 60 – 70 nm is more effective in reducing the content of exchangeable Cd in soil than zeolite with a particle size of 149 μm [31]. In this regard, the mechanochemical method [32] is of great practical interest to improve the properties of modified zeolites [32, 33], including as a way to produce slow-release fertilizers [28, 34, 35]. Treatment of clinoptilolite with NH_4Cl and mechanochemical activation of clinoptilolite/phosphate rock (ratio 20/1) for 120 min increased the availability of P_2O_5 more than tenfold [36]. The phosphorus-zeolite fertilizer resulted from the combined air-dry and wet grinding of ore and zeolite [37]. Mechanochemical treatment of double layered hydroxides with potassium hydrophosphate in a molar ratio of 2 : 1 for 9 hours gives potential stable fertilizers [34], and kaolin with KH_2PO_4, K_2HPO_4, and K_3PO_4 for two hours gives fertilizers with delayed release of K^+, PO_4^{3-} ions [28].

In addition to modified mineral additives, innovative multicomponent fertilizers with controlled release of nutrients resulted from organic polymers. For example, composites of polyvinyl alcohol with $FePO_4$ [38], polyvinyl alcohol with polyacrylamide [39], polyvinyl alcohol, polyvinylpyrrolidone, epoxy resin, and zeolite [40], as well as hydrogel based on bagasse and nanozeolite [41]. Superabsorbing polymers are of particular interest for plant growth and water retention in light soils [42], and interpolymer complexes are of particular interest for increasing resistance to water erosion [43,44].

Forage perennial legume grasses are the most important component of agricultural systems in temperate climatic conditions [45]. The aim of the present work was to investigate the effect of mechanically activated clinoptilolite zeolite, clinoptilolite zeolite with sodium and ammonium hydrophosphates, as well as the interpolymer complex polyvinyl alcohol/polyacrylamide filled with mechanically activated clinoptilolite zeolite on the growth of perennial legume grasses in grey forest soil.

2. Experimental

2.1. Materials

Dark grey forest soil was used as a test soil, samples of which were taken in the city of Chita and near Lake Arakhley (Transbaikal Territory, Russia). The soil samples contain the following elements, in milligrams per kilogram: sodium (211.0 ± 4.2) / (333.0 ± 2.8); potassium (2402.5 ± 7.8) / (4208.5 ± 4.9); magnesium (1770.0 ± 4.2) / (3150.0 ± 2.8); calcium (236.5 ± 3.5) / (1717.0 ± 4.2); manganese (514.4 ± 3.8) / (403.0 ± 0.3); cobalt (3.5 ± 0.2) / (2.7 ± 0.1); nickel (5.6 ± 0.1) / (4.3 ± 0.1); copper (11.7 ± 0.0) / (8.6 ± 0.1); zinc (94.6 ± 0.1) / (56.8 ± 0.0); cadmium (0.17 ± 0.01) / (0.06 ± 0.01); lead (12.2 ± 0.3) / (5.7 ± 0.3); and arsenic (0.24 ± 0.01) / (0.28 ± 0.01) for Chita and Arakhley, respectively. The metal content is higher in the Chita soil sample except for alkaline metals (Na, K) and alkaline earth metals (Ca, Mg). The aqueous soil extracts from Chita and Arakhley were found to have a neutral pH, with medium acidity levels of 7.63 ± 0.20 and 7.15 ± 0.20, respectively. Experiments with mineral and organo-mineral zeolite-containing additives were conducted in laboratory conditions on Chita and Arakhley soil samples, respectively. One gram of mineral fertilizer was added to 680 cm^3 soil samples and seeds of perennial legume grasses pre-germinated in a small amount of water were planted in them. Soil without any additives was used as a control, and the ratio of zeolite-organic fertilizer to soil was 1 : 7 wt % [44]. The duration of the experiment was 29 days.

Natural zeolites were clinoptilolite and clinoptilolite-stilbite rocks of the Shivyrtuy and Kholinsky deposits, respectively (Transbaikal Territory, Russia). The phase and chemical composition of these rocks was studied earlier [46]. As inorganic additives, we used sodium dodecahydrate hydrophosphate (analytical grade, Russia) and ammonium hydrophosphate (analytical grade, Russia). As organic additives we used polyvinyl alcohol (PVA, lot 02-1799, China) and polyacrylamide (PAA, lot 130617, China). The viscosity of a 0.25 % PAA solution in a 3 % sodium chloride solution at 30 °C is at least 2.2 mm^2s^{-1}; density, 1.302 $g \cdot cm^{-3}$; pH value 7 – 13; glass transition temperature, 190 °C. The viscosity of PVA is 22 – 30 mPa s; density, 1.290 $g \cdot cm^{-3}$; pH value 5 – 7; glass state temperature, 75 – 85 °C.

Seeds of perennial legume grasses, namely meadow clover (*Trifolium pratense*), eastern galega (*Galega orientalis*) and sand sainfoin (*Onobrychis arenaria*), were used as test objects.

2.2. Mechanical treatment of clinoptilolite zeolite and preparation of phosphorus-zeolite fertilizers

Mechanochemical activation of air-dried clinoptilolite zeolite alone and as well as an equimass mixture of mineral fraction (particle size is not more than 0.5 mm) of clinoptilolite-stilbite (I) or clinoptilolite (II) rocks with sodium hydrophosphate dodecahydrate (a) or ammonium hydrophosphate (b) was carried out with the help of a vibrating sample grinder IVS-4 (75T-DRM), Russia. The minimum size of material after grinding is less than 0.1 mm, the frequency is 23.4 Hz, the power is 0.6 kW, the mass of grinding steel bodies is 0.87 kg. Duration of mechanical activation is 10 minutes [46], which corresponds to the dose of mechanical energy

$$D = J \cdot t = 4 \cdot 600 = 2.4 \text{ kJ} \cdot \text{g}^{-1}, \quad (1)$$

where the energy intensity (J) of the vibrating sample grinder IVS-4 is 4 $W \cdot g^{-1}$, and the grinding time (t) is 600 s.

2.3. Preparation of zeolite-organic fertilizers

Natural zeolite-containing rocks were crushed for 2 min in a BOYD MK III crusher (ROCKLABS, New Zealand) and subjected to mechanical activation for 3 min in an Essa LM2 Pulverising Mill (Essa, USA), which corresponds to a dose of mechanical energy of 3.8 $kJ \cdot g^{-1}$. The particle size after three minutes of abrasion of the mineral powder is up to 75 μm, the frequency is 50 Hz, the power is 2.20 kW, and the revolutions speed is 900 rpm. From the resulting powder, a highly dispersed fraction with a particle size not exceeding 71 μm was separated by the sieve method. The polyvinyl alcohol/polyacrylamide interpolymer complexes were obtained by mixing equal volumes of aqueous solutions of initial polymers with concentrations 1, 2, and 4 g·dL^{-1} [47]. Filling of these interpolymer complexes with highly dispersed clinoptilolite zeolite powder was carried out at 25 °C under stirring with a magnetic stirrer for 20 minutes.

The labelling of these samples includes the concentration of the polyvinyl alcohol solution (1, 2, or 4 g·dL^{-1}) in the interpolymer complex (the concentration of the polyacrylamide solution is 4 g·dL^{-1}) and the type of zeolite (I or II) in the mineral filler.

2.4. Methods of characterization

The specific gravity was measured using the pycnometer method.

The specific surface area and air permeability were determined using the Tovarov method.

The resistance of samples in aqueous suspensions with mass fractions of dispersed phase 0.4 and 4.0 wt % was measured using a conductometer K 1-4 UPK UPI at a frequency of 1 kHz and at different values of temperature maintained by a laboratory thermostat-reducer LTR-24.

IR spectra were recorded by using a SHIMADZU FTIR-8400S FTIR spectrometer in the region from 4000 to 400 cm^{-1} on films cast in air at 25 °C from aqueous solutions. The ratio of intensities of absorption bands in the regions 1140 – 1144 and 1092 – 1098 cm^{-1} was calculated as the ratio of the lengths of the segments from the maxima of these absorption bands to the tangent to the wings of the spectral contour in the region 939 – 1180 cm^{-1}. The degree of crystallinity of polyvinyl alcohol was calculated according to the equation [48]:

$$\alpha,\ \% = -13.1 + 89.5(A_{1144}/A_{1094}). \quad (2)$$

The acidity of the medium (pH) of aqueous soil extracts was determined according to GOST 26423-85.

Distribution of mineral filler in zeolite-organic aqueous suspension was studied after their application on glass substrates and solvent evaporation at 25 °C after 72 hours by optical microscopy. A research ZOOM-stereomicroscope RZ with a smooth magnification function (Meiji Techno, Japan) and a sample image magnification of 150× was used for this purpose.

Optical densities of polymer suspensions with concentrations of 1, 2, and 4 g·dL^{-1} were measured at a wavelength of 440 nm at 25° using a KFK-2 photoelectric colorimeter in cells 3 cm thick using distilled water as a reference solution. The turbidity of the suspensions was calculated using the following formula:

$$\tau = 2.303 \cdot A_{440}/l, \quad (3)$$

where A_{440} is the optical density at a wavelength of 440 nm, and l is the length of the optical path, cm.

Seed germination of perennial legume grasses was studied according to GOST 12038-84 and determined as a percentage (%) representing the ratio of germinated seeds to the total number of planted seeds. Stem length was measured using a millimeter ruler with an absolute error of ± 0.5 mm, and results were presented as mean ± SD.

Dry weight of the above-ground parts of the studied grasses was determined using a gravimetric method with scales having an error of ± 0.01 g.

Phytotoxic effect was determined by the bioparameter of plant stem length [49]. The phytotoxicity index (P, %) was calculated according to the following formula:

$$P = \frac{B_c - B_i}{B_c} \cdot 100\,\%, \quad (4)$$

where B_c is the mean value of the bioparameter for the control sample, and B_i is the mean value of the bioparameter for the test sample.

Correlation coefficients between plant bioparameters and physical characteristics of fertilizers were calculated using MS Excel.

3. Results and discussion

We established that mechanical activation leads to the amorphization of clinoptilolite and the formation of hydrogen bonds between hydrophosphates (HPO_4^{2-}) and the oxygen atoms of the alumino-silicate framework [46] (Fig. 1).

The latter fact is consistent with the data on the adsorption of these ions on clinoptilolite [25]. The blue shift of the absorption bands due to asymmetric vibrations of alumino-silicon tetrahedra in the IR spectra of samples I, II, and Ia, Ib, IIa [46] indicates the quantum-size effect and substitution of aluminum and silicon for phosphorus, respectively.

Composition and physical characteristics of mechanically activated zeolites and mechanically activated equimass mixtures of zeolites with sodium and ammonium hydrophosphates are given in Table 1.

As a result of modification of clinoptilolite-stilbite and clinoptilolite rocks with sodium hydrophosphate, their hygroscopic humidity increases by 1.2 and 1.4 times (samples Ia and IIa), respectively. When ammonium hydrophosphate is used, this index, on the contrary, decreases in both cases by 1.3 times. Hydrated intra-framework cations contained within the nanoporous zeolite framework will affect their electrophysical properties. The electrical conductivity of aqueous zeolite suspension is known to affect the germination of tomatoes [50]. In this case, the use of samples Ib and IIb as fertilizers can result in the best seed germination, as the values of electrical conductivity of their suspensions are the highest. However, the specific surface area, depending on the dispersity of solid particles, is the highest in mechanically

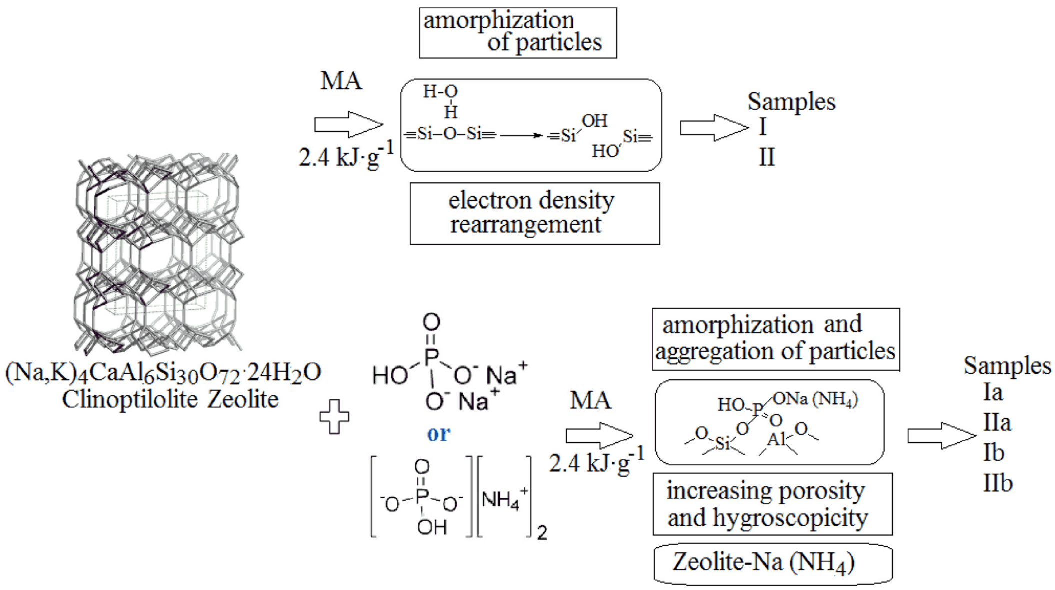

FIG. 1. Schematic representation of processes occurring due to mechanical activation of clinoptilolite zeolites and their mixture with sodium and ammonium hydrophosphates [46]: MA – mechanical activation; I – clinoptilolite-stilbite rock; II – clinoptilolite rock; a – $Na_2HPO_4 \cdot 12H_2O$; b – $(NH_4)_2HPO_4$

TABLE 1. Content and characteristics of mechanically activated zeolite and phosphorus-zeolite fertilizers (mechanical energy dose 2.4 kJ·g^{-1})

Ferti-lizers	Content, wt %		W, wt. % [46]	γ, g·cm^{-3}	Specific surface area, m^2·g^{-1}		Electrical conductivity of aqueous suspension of fertilizers with solid phase 4/0.4 wt %, EC, mS·cm^{-1}		
	Zeoli-tes	Salt			BET [46]	as per Tovarov	24 °C	32 °C	41 °C
I	100	0	3.9	2.06	32.3	2.54	0.09/0.07	0.10/0.09	0.15/0.15
Ia	50	50	4.7	2.08	1.9	1.56	13.25/7.29	14.58/8.33	15.35/10.41
Ib	50	50	3.7	1.78	8.3	0.60	17.67/8.33	18.81/11.66	24.30/11.66
II	100	0	4.2	1.99	22.2	2.30	0.12/0.09	0.18/0.12	0.24/0.16
IIa	50	50	6.0	2.12	2.2	1.45	13.56/8.33	16.66/8.33	19.44/12.68
IIb	50	50	3.3	1.78	5.2	0.92	16.66/8.33	20.11/11.66	23.33/11.22

I – clinoptilolite-stilbite rock; II – clinoptilolite rock; a – $Na_2HPO_4 \cdot 12H_2O$; b – $(NH_4)_2HPO_4$;

BET – the Brunauer–Emmet–Teller model [46]; as per Tovarov – air permeability specific surface; γ – specific gravity

activated natural zeolites I and II, and this may also be important for seed germination. A decrease in specific surface area indicates an increase in particle size and the formation of aggregates. At the same time, the most significant decrease in specific gravity and air permeability specific surface is observed due to the mechanoactivation of zeolites with ammonium hydrophosphate (samples Ib, IIb). Interestingly, the dependences of electrical conductivity of aqueous suspensions of modified zeolites depend rather strongly on this specific surface area (correlation coefficients r_{xy} are -0.91 and -0.96 for 0.4 and 4.0 wt % suspensions, respectively, at 24 °C).

Experimental data on the effect of mechanically activated clinoptilolite rocks and phosphorus-zeolite fertilizers on bioparameters of perennial grasses are given in Table 2.

The electrical conductivity of aqueous suspensions of zeolite fertilizers was found to moderately affect the stem length of meadow clover (*Trifolium pratense*), sand sainfoin (*Onobrychis arenaria*), and the mass of the above-ground part of meadow clover (*Trifolium pratense*).

The correlation coefficients of 0.59 and 0.57 showed that the air permeability specific surface of the samples had a moderate effect on the stem length of eastern galega (*Galega orientalis*) and the mass of the above-ground part of sand

TABLE 2. The effects of clinoptilolite zeolite and phosphorus-zeolite fertilizers on bioparameters of perennial grasses

Perennial grasses	Soil (control)	Soil with fertilizers					
		I	Ia	Ib	II	IIa	IIb
Seed germination, %							
Meadow clover	80	54	49	77	80	80	54
Eastern galega	75	25	30	25	100	90	40
Sand sainfoin	40	27	20	0	7	27	20
Stem length, mm							
Meadow clover	121 ± 3	120 ± 5	90 ± 3	113 ± 3	128 ± 4	108 ± 6	110 ± 3
Eastern galega	139 ± 4	110 ± 3	125 ± 1	132 ± 2	163 ± 2	123 ± 4	107 ± 1
Sand sainfoin	94 ± 2	100 ± 2	117±2	0	105 ± 0	91 ± 1	98 ± 1
Weight of above-ground part, g							
Meadow clover	4.20	4.02	1.52	3.25	3.12	3.44	2.02
Eastern galega	4.94	1.44	1.71	2.39	4.78	4.05	1.98
Sand sainfoin	0.68	0.63	0.50	0	0.15	0.41	0.28
Phytotoxicity index, %							
Meadow clover	—	1	26	7	−6	11	9
Eastern galega	—	21	10	5	−17	12	23
Sand sainfoin	—	−6	−24	100	−12	3	−4

sainfoin (*Onobrychis arenaria*). In addition, the specific weight is moderately correlated with the seed germination and the length of the stem of sand sainfoin (*Onobrychis arenaria*), and it also has a strong effect on the mass of the above-ground part of this perennial plant. The correlation coefficients -0.75, 0.72, and 0.66 showed that the specific surface area, as determined by the BET method of the samples strongly influenced the stem length of meadow clover (*Trifolium pratense*), eastern galega (*Galega orientalis*), and the mass of the above-ground part of meadow clover (*Trifolium pratense*). Data analysis confirms ($r_{xy} = 0.55$) that hygroscopic humidity moderately affects seed germination and mass of the above-ground part of eastern galega (*Galega orientalis*). Thus, the possible influence of electrical conductivity of aqueous suspensions of zeolites on germination of seeds of perennial leguminous plants has not been experimentally confirmed. This may be due to the long storage of seeds before planting. However, the observed effect of the specific surface area of zeolites on plant stem length still indicates the efficiency of zeolite application as fertilizers.

It was found that the seed germination of eastern galega (*Galega orientalis*) compared to the control soil sample without fertilizer (Soil) was 33 and 20 % higher for the soil with fertilizer based on clinoptilolite rock (sample II) and clinoptilolite rock with sodium dodecahydrate hydrophosphate (sample IIa), respectively. The germination of meadow clover (*Trifolium pratense*) seeds for these samples (samples II and IIa) is the same as in soil without fertilizer (Soil). For seeds of sand sainfoin (*Onobrychis arenaria*), fertilizer application contributes to the deterioration of germination, and in soil with clinoptilolite rock and ammonium hydrophosphate (sample Ib), seeds did not germinate at all.

The absence of satisfactory results with the rest of the samples is probably connected with aggregation of particles (Fig. 1) and a decrease in specific surface area of samples Ia, Ib, IIa, IIb by 4...16 times (Table 1) in comparison with mechanically activated clinoptilolite zeolites (samples I, II). It was revealed that the application of mineral phosphorus-zeolite fertilizers into the soil, as a rule, depresses the growth of meadow clover (*Trifolium pratense*) and eastern galega (*Galega orientalis*). This is reflected in a lower value of average stem length (Table 2). At the same time, phytotoxicity (phytotoxicity index $P > 20$ %) is shown by samples Ia and I; IIb and Ib in relation to meadow clover (*Trifolium pratense*) and eastern galega (*Galega orientalis*), and sand sainfoin (*Onobrychis arenaria*), respectively. The exception is the addition of mechanically activated clinoptilolite rock (sample II) to the soil. This fertilizer contributes to the increase of average stem length value and a low phytotoxicity indexes ($P < 0$ %) for all investigated perennial legume grasses by

6...17 % in the following order:

$$\textit{meadow clover} < \textit{sand sainfoin} < \textit{eastern galega}. \quad (5)$$

For sand sainfoin (*Onobrychis arenaria*), the application of phosphorus-zeolite fertilizers shows an increase in the average value of stem length and low phytotoxicity index ($P < 0$ %) for all samples except two of them – Ib, IIa. The highest increase in stem length, by 24 %, occurs for fertilizer made from clinoptilolite-stilbite rock with sodium hydrophosphate dodecahydrate (sample Ia).

In terms of the weight of the above-ground plant parts, all resulting values in fertilized soil are lower than the same values in unfertilized soil. Among the studied data, the best results for meadow clover (*Trifolium pratense*) and sand sainfoin (*Onobrychis arenaria*) were observed when mechanically activated clinoptilolite-stilbite rock (sample I) was applied as a fertilizer, and for eastern galega (*Galega orientalis*) – when mechanically activated clinoptilolite rock was applied (sample II).

Therefore, according to the experimental results obtained, mechanically activated clinoptilolite zeolite rock has an almost maximum specific surface area and air permeability, and, obviously, the smallest particle size. It can be recommended for improving the growth of perennial legume grasses in grey forest soil.

The interpolymer complex polyvinyl alcohol/polyacrylamide [51] is promising for preventing soil erosion [45] and retaining moisture in it, and its combination with mechanically activated clinoptilolite rock can obviously have a synergistic effect. Previously, we obtained polyvinyl alcohol/polyacrylamide/clinoptilolite nanocomposites with coagulation-type structure and fairly uniform distribution of mineral filler in the polymer matrix [47]. Aggregates of anisodiametric polymer structures are able to form upon cooling of polyvinyl alcohol solution. Highly dispersed clinoptilolite zeolite particles added to the polymer system can play the role of crystallization centers. This structuring effect is observed to the greatest extent in the optical image of the film resulting from sample 4^{II} – equal volumes of aqueous solutions of PVA and PAA with concentrations of 4 g·dL^{-1} each, filled with 0.4 wt % mechanically activated clinoptilolite rock (Fig. 2).

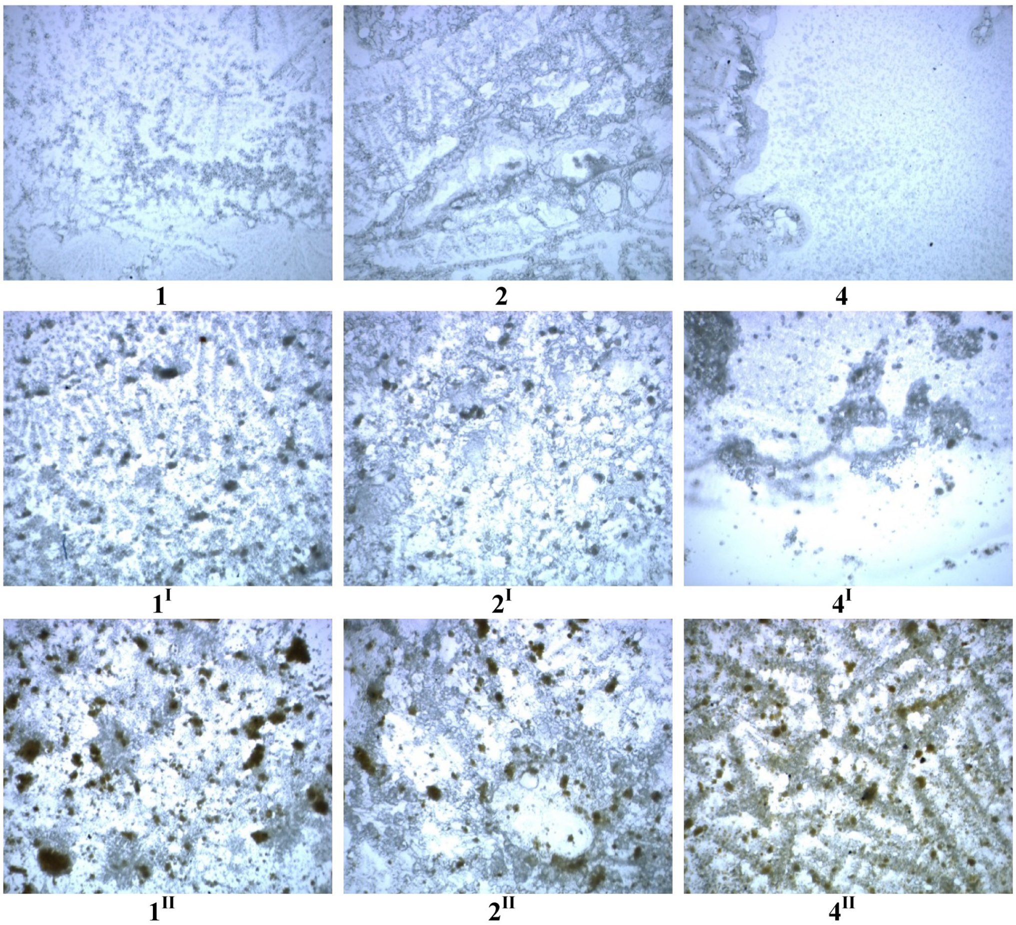

FIG. 2. Optical micrographs of the unfilled and filled 0.4 wt % clinoptilolite-stilbite (I) and clinoptilolite (II) interpolymer complex films obtained from water solutions with concentrations of polyvinyl alcohol of 1; 2; 4 g·dL^{-1} and polyacrylamide of 4 g·dL^{-1} (field of view 1.8 mm; magnification: 150×)

The interaction between polymers during the formation of the interpolymer complex can be conveniently studied using infrared spectroscopy [51]. The IR spectra of the PVA/PAA interpolymer complexes with mechanically activated clinoptilolite-stilbite and clinoptilolite zeolite fillers are shown in Figs. 3 and 4. It was found that a shift of some characteristic absorption bands is observed in the IR spectra of the filled clinoptilolite zeolite interpolymer samples (Fig. 3).

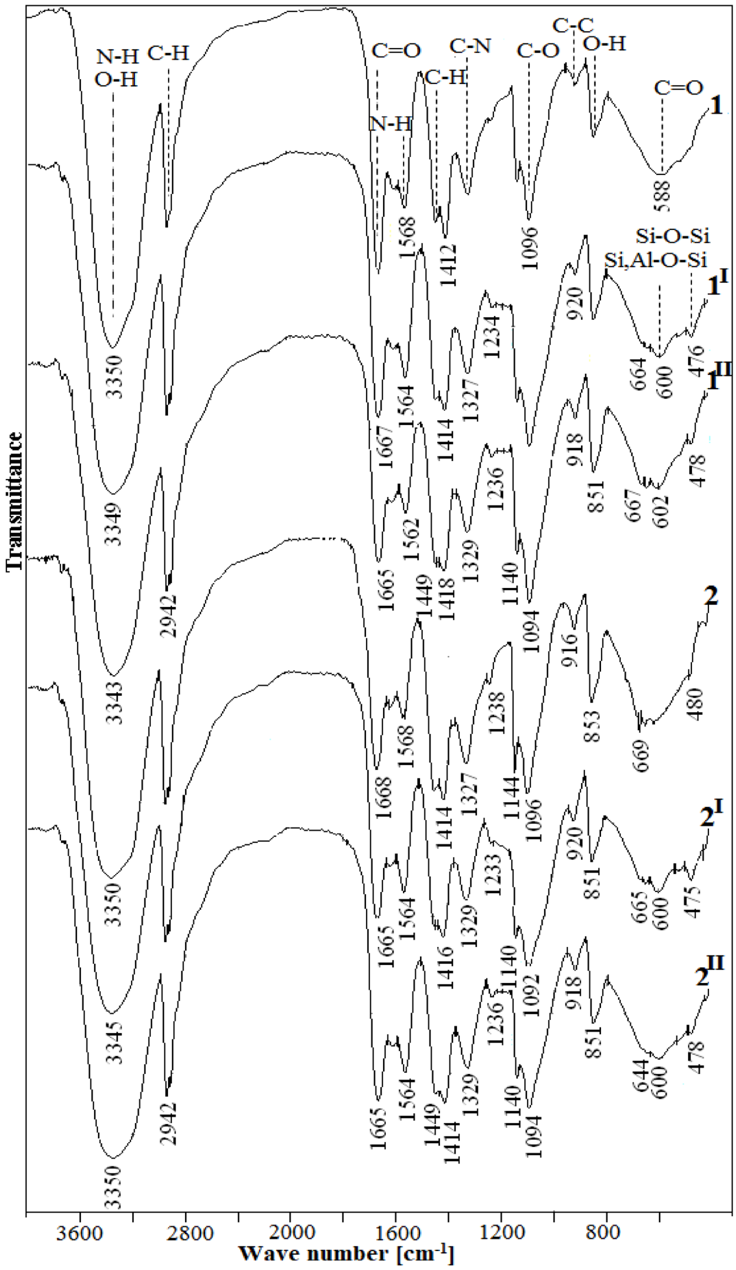

FIG. 3. IR spectra of the unfilled and filled clinoptilolite zeolite interpolymer complexes resulting from mixing equal volumes of aqueous solutions of 1 or 2 g·dL^{-1} polyvinyl alcohol and 4 g·dL^{-1} polyacrylamide

There is a decrease in the frequencies of maxima of absorption bands caused by valence vibrations of O–H, N–H bonds in the region of 3340...3350 cm^{-1}, as well as deformation vibrations of N–H bonds in the region of 1560...1570 cm^{-1}. In addition, the absorption bands corresponding to deformation vibrations of C–H bonds in the region of 1410...1420 cm^{-1} are shifted towards higher frequencies. In the IR spectra of samples 1^{I} and 1^{II} the maxima of absorption bands with frequencies characteristic for clinoptilolite zeolites ($\sim$ 670; 600; 480 cm^{-1}) appear [46]. It should be noted that the shifts of absorption bands are larger when the interpolymer complex is filled with clinoptilolite than with clinoptilolite-stilbite rock (samples 1^{I} and 1^{II}, Fig. 3).

A two-fold increase in the concentration of polyvinyl alcohol in the PVA/PAA interpolymer complex favours a slight shift by 2 – 4 cm^{-1} of the individual absorption bands, usually to the low-frequency region (sample 2, Fig. 3). Filling with clinoptilolite zeolite leads to a larger shift of absorption bands in the case of clinoptilolite-stilbite rock (sample 2^{I}, Fig. 3).

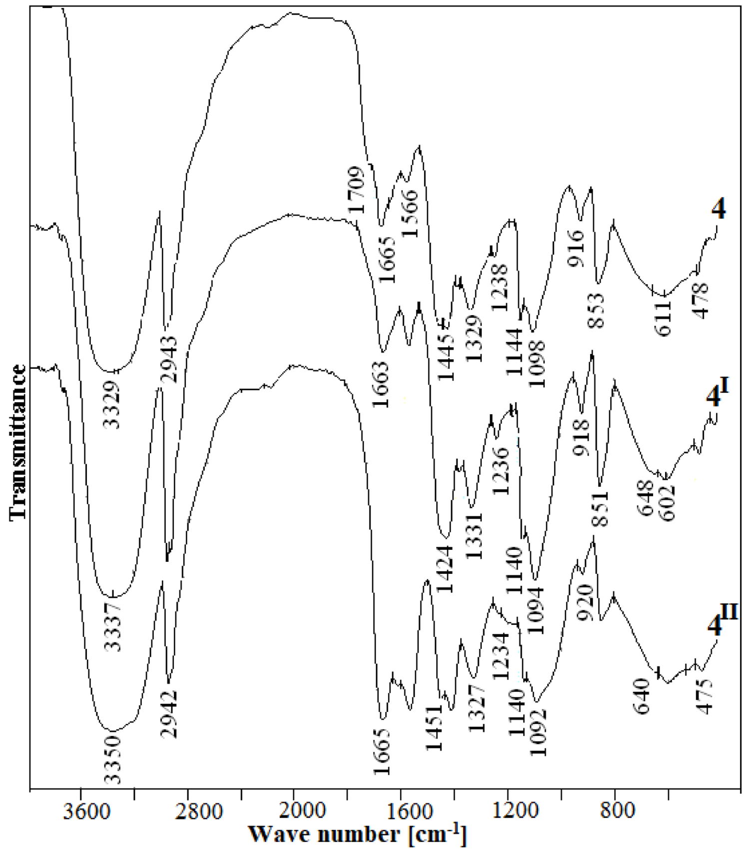

FIG. 4. IR spectra of the unfilled and filled clinoptilolite zeolite interpolymer complexes resulting from mixing equal volumes of aqueous solutions of 4 g·dL^{-1} polyvinyl alcohol and 4 g·dL^{-1} polyacrylamide

Further increase of polyvinyl alcohol content from 2 to 4 g·dL^{-1} in the interpolymer complex causes the appearance of a shoulder at 1709 cm^{-1} in the infrared spectrum related to the valence vibrations of the carbonyl group (sample 4, Fig. 4).

In addition, shifts towards low frequencies of the absorption band at 3329 cm^{-1}, corresponding to the valence vibrations of O–H and N–H, as well as shifts by 2 – 4 cm^{-1} of the maximums of the absorption bands due to the valence vibrations of the carbonyl group and deformation vibrations of N–H, C–H are registered. The absorption bands corresponding to deformation vibrations of C–H, C–N bonds and valence vibrations of C–O in the regions 1414...1418; 1327...1329 and 1096...1098 cm^{-1}, respectively, are shifted to the high-frequency region. Such changes are explained by association processes of macromolecules with the help of functional groups C=O, NH_2, OH, which is in agreement with the authors' data [51]. Filling of the PVA/PAA interpolymer complexes with clinoptilolite is also reflected in IR spectra by shifts of absorption bands corresponding to N–H, O–H, C–N, C–O, C–C vibrations (samples 4^{I} and 4^{II}, Fig. 4). Moreover, in these cases, significant changes in the characteristic absorption bands related to the carbonyl group C=O are observed – a decrease in the intensity of the absorption band with a maximum at 1663 cm^{-1} (sample 4^{I}, Fig. 4) and an increase in the intensity of the absorption band with a maximum at 1665 cm^{-1} (sample 4^{II}, Fig. 4). A slight shift in the maxima of the absorption bands at 916 and 853 cm^{-1} corresponding to the bending and torsional vibrations of the C–H of polyvinyl alcohol (sample 4, Fig. 4) is also accompanied by a change in intensity – an increase (sample 4^{I}, Fig. 4) and a decrease (sample 4^{II}, Fig. 4). In all IR spectra of zeolite-organic samples, a shoulder at 1171...1177 cm^{-1} appears, which can be attributed to the valence vibrations of Al(Si)–O_4 in clinoptilolite zeolite [46].

Taking into account the presence of surface silanol groups Si–OH in mineral filler, amide and carbonyl groups in polyacrylamide, and hydroxyl groups in polyvinyl alcohol, changes in IR spectra of filled polymer samples confirm the formation of organo-mineral complexes (Fig. 5).

The results obtained by infrared spectroscopy are in agreement with optical microscopy data (Fig. 2) and open prospects for the use of sample 4^{II} as a fertilizer. One factor that can influence seed germination is the association of polymeric macromolecules in solutions, which can be conveniently monitored by measuring turbidity. Another influential factor to be highlighted is the degree of crystallinity of the polymer, as amorphous regions may favour greater nutrient availability. The composition of organo-zeolite fertilizers, filler fraction (φ) in optical images of polymer films, turbidity, ratio of absorption band intensities in IR spectra (A_{1144}/A_{1094}), and degree of crystallinity of polyvinyl alcohol (α_{PVA}) are given in Table 3.

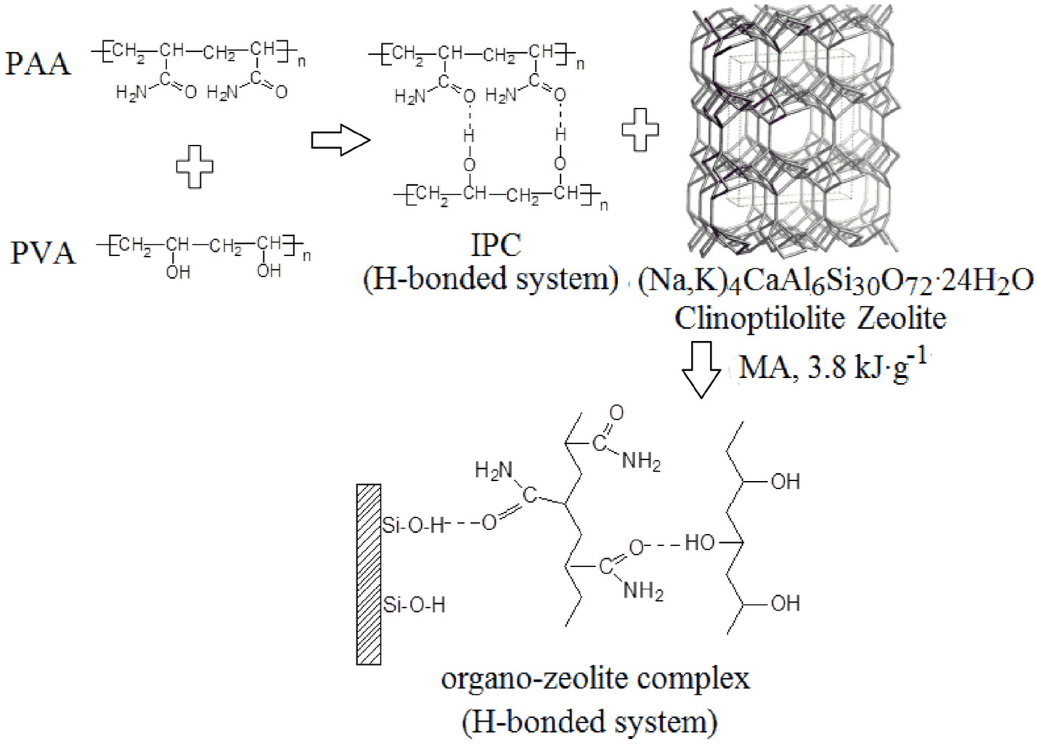

FIG. 5. Scheme for preparation of polyvinyl alcohol/polyacrylamide interpolymer complex (IPC) filled with mechanically activated (MA) clinoptilolite zeolite

TABLE 3. Composition and characteristics of zeolite-organic fertilizers

Fertilizers	Composition				φ [47]	Turbidity, τ, cm^{-1}	$\frac{A_{1144}}{A_{1094}}$	α_{PVA}, %
	Concentration, g·dL^{-1}		Zeolite					
	PVA	PAA	wt. %	type				
1	1	4	0	—	0	0.046	0.67	46.9
1^{I}	1	4	0.4	Cl, St	0.10	0.768	0.65	45.1
1^{II}	1	4	0.4	Cl	0.14	0.368	0.64	44.2
2	2	4	0	—	0	0.085	0.80	58.5
2^{I}	2	4	0.4	Cl, St	0.10	0.430	0.69	48.7
2^{II}	2	4	0.4	Cl	0.15	0.729	0.71	50.4
4	4	4	0	—	0	0.146	0.82	60.3
4^{I}	4	4	0.4	Cl, St	0.18	0.614	0.78	56.7
4^{II}	4	4	0.4	Cl	0.31	0.576	0.74	53.1

Cl – Clinoptilolite, St – Stilbite

It is easy to see that the addition of zeolite filler to the interpolymer complex expectedly increases turbidity by 4 – 9 and 4 – 17 times for clinoptilolite and clinoptilolite-stilbite rocks, respectively. The distribution of zeolites in interpolymer complexes (1; 2; 4) was found to be more homogenous for clinoptilolitic rocks. It should be noted that the structure of samples 2^{I}, 2^{II}, 4^{II} is characterized by a decrease in the degree of crystallinity of polyvinyl alcohol by more than 10 % compared to that for unfilled samples. According to the obtained results, the preference should be given to clinoptilolite rock over clinoptilolite-stilbite rock.

Changes in seed germination and stem length of the studied perennial legume grasses under the influence of zeolite-organic fertilizers, as well as the values of correlation coefficients, are presented in Table 4.

TABLE 4. The effects of zeolite-organic fertilizers on bioparameters of perennial grasses

Perennial grasses	Soil (control)	Soil with fertilizers					
		1^{I}	2^{I}	4^{I}	1^{II}	2^{II}	4^{II}
Seed germination, %							
Meadow clover	100	67	75	58	50	25	92
Eastern galega	17	50	50	75	42	17	33
Sand sainfoin	25	25	33	33	92	33	58
Stem length, mm							
Meadow clover	90 ± 3	46 ± 3	46 ± 2	49 ± 3	30 ± 4	77 ± 4	93 ± 4
Eastern galega	48 ± 2	63 ± 4	64 ± 3	38 ± 2	33 ± 2	17 ± 2	80 ± 4
Sand sainfoin	62 ± 3	42 ± 2	42 ± 3	55 ± 3	30 ± 3	77 ± 3	93 ± 5
Phytotoxicity index, %							
Meadow clover	—	49	49	46	67	14	−3
Eastern galega	—	−31	−33	21	31	65	−67
Sand sainfoin	—	32	32	11	52	−24	−50

It was found that turbidity of polymer-mineral suspensions strongly ($r_{xy} = -0.71$) affects only the germination of seeds of sand sainfoin (*Onobrychis arenaria*). In addition, the degree of crystallinity of polyvinyl alcohol only moderately ($r_{xy} = 0.52$ and 0.62) affects the stem length of meadow clover (*Trifolium pratense*) and sainfoin (*Onobrychis arenaria*).

It was found that zeolite-organic fertilizers most of all promoted germination of eastern galega (*Galega orientalis*) and sand sainfoin (*Onobrychis arenaria*), but worsened germination of meadow clover (*Trifolium pratense*) seeds. At the same time, the soil fertilized with sample 4^{II} performed better than the others, although it was inferior to the control sample in terms of germination of meadow clover (*Trifolium pratense*) seeds by 8 %. When fertilizer 4^{II} was used, the phytotoxicity index was negative and the average value of perennial legume grasses' stem length increased by 67; 50; 3 % for eastern galega (*Galega orientalis*), sand sainfoin (*Onobrychis arenaria*), and meadow clover (*Trifolium pratense*) compared to the control. Fertilizer 2^{II} improves the growth of sand sainfoin (*Onobrychis arenaria*) by 24 %, and fertilizers 1^{I}, 2^{I}, at the same time, increase the stem length of eastern galega (*Galega orientalis*) by $\sim$30 % in relation to the soil without fertilizer. Consequently, according to the totality of the conducted experiments, it is possible to recommend the PVA/PAA interpolymer complex resulting from mixing equal volumes of aqueous solutions of these polymers with concentrations of 4 g$\cdot$dL^{-1} each, filled with 0.4 wt % clinoptilolite rock mechanically activated for three minutes to improve germination and growth of perennial legume grasses in grey forest soil.

The obtained results of the effect of zeolite fertilizers on the growth of perennial leguminous plants confirmed the important role of the size factor, as the specific surface area of powder and turbidity of suspensions depend on the dispersity of particles.

4. Conclusions

Thus, the application of mineral and organo-mineral fertilizers to forest grey soil promotes better germination and growth of perennial legume grasses such as meadow clover (*Trifolium pratense*), eastern galega (*Galega orientalis*), and sand sainfoin (*Onobrychis arenaria*). The fertilizers used were clinoptilolite zeolite rock, mechanically activated for 10 minutes in the vibrating sample grinder IVS-4 (mechanical energy dose 2.4 kJ$\cdot$g^{-1}), and the interpolymer complex of polyvinyl alcohol/polyacrylamide was created by mixing equivolume parts of aqueous solutions of polymers with concentrations of 4 g$\cdot$dL^{-1} each, and filling it with 0.4 wt % of mechanically activated clinoptilolite rock for 3 minutes in an Essa LM2 Pulverising Mill (mechanical energy dose 3.8 kJ$\cdot$g^{-1}). These clinoptilolite zeolite and zeolite-organic fertilizers show promise in solving agrochemical problems. Using correlation analysis, it was established that the determining factors affecting the stem length of meadow clover (*Trifolium pratense*) and eastern galega (*Galega orientalis*) are the specific surface area of powder zeolite fertilizers. A significant parameter of fertilizers from polymer-zeolite suspensions for the growth of sand sainfoin (*Onobrychis arenaria*) is their turbidity.

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