The use of natural sorbents in the technology of obtaining a source of trace element additives in the soil

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Abstract. Molybdenum-containing non-traditional fertilizers based on zeolite tuff of the Kholinsky deposit were obtained by sorption method. The main stages of the production technology: granulation-screening with a grain diameter of 1÷2 mm; modification with molybdenum (VI) ions. Molybdenum-containing zeolite tuffs of the Kholinsky Deposit increase the yield of peas by a green mass.

1 Introduction

The food crisis, along with the overpopulation crisis, is one of the global environmental problems of the planet.

There are two main ways to solve the food problem: extensive and intensive. The extensive route involves the production of food through the expansion of agricultural land. This way of solving the problem is not promising. Suitable land for agriculture is limited on the planet today. There are no free suitable lands for development, practically. According to the U.S. Geological Survey, arable land makes up only 12.6% of the land surface. The remaining 87.4% is land that, due to climatic conditions or soil composition, cannot be used for traditional agriculture (i.e. mountains, deserts, permafrost, etc.).

An intensive way to solve the food problem involves mechanization, chemization, irrigation of agriculture, as well as increasing its energy capacity, and the use of new high-yielding crop varieties. Intensification of agriculture leads to the yields increasing. At the same time, intensification accelerates the removal of nutrients from the soil and the mineralization of humus. Regulation of these processes is made possible by applying fertilizers.

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The Food and Agriculture Organization (FAO) analysed the increasing in agricultural production and the effectiveness of agrochemicals usage. Based on this estimate, Food and Agriculture Organization (FAO) forecasts an increase in the level of consumption of basic mineral fertilizers to 188 million tons by 2030. However, there is a danger that excessive use of them can lead to pollution of the earth and air, the emission of greenhouse gases, thereby creating a risk to human health and the environment. Therefore, it is important to combine advanced farming practices with environmentally friendly technologies.

One of the promising approaches to reducing the anthropogenic impact on the soil and technogenic pollution of the environment is the enrichment of the soil with minerals that increase their absorption properties. Such minerals include natural sorbents zeolite-containing rocks, perlites, glauconite Sands, bentonite and palygorskite clays (Table 1). These minerals, due to their cost-effectiveness and good absorption properties, are widely used in various industries for separation and extraction of valuable components, treatment of gas emission and industrial effluents, desalination of drinking water and in pharmaceuticals [1-11], in animal husbandry and agriculture [12-14] (Table 1).

Table 1. Possible use of non-traditional minerals in agriculture

application sphere	zeolite,	bentonite	glauconite	palygorskite	vermiculite	peat vivianite	synnyrite	diatomite & rafterstone	perlite
agriculture									
Liming, fertilizing fields		+	+		+	+	+		
Structurization		+		+					
Soil adsorption of pesticides, toxic substances (heavy metals, radionuclides)	+	+	+	+				+	
Regulation of water exchange in the soil	+	+	+	+				+	
Decrease in soil acidity	+								
Soil reclamation			+						
Seed granulation				+	+			+	
Hydroponic materials	+			+	+	+			+
Animal husbandry									
Feed additives	+	+		+	+				
Fish growth additives&water treatment	+		+						
Litter	+			+	+				
Wastewater treatment & deodorization	+	+	+					+	
Growing Chlorella for fodder	+		+						

Examples of diatomites using show an improvement in soil quality and yield increasing when growing carrots [15-16]. Experiments with bentonite additives improved the performance of sandy and sandy loam soils and increased the yield of corn and millet grains [17-18]. The addition of glauconitolite significantly increases the yield of wheat, corn, oats, and beetroot [19-20]. Successful studies have also been conducted in various countries using diatomite, palygorskite, and bentonite clay for corn, wheat, potatoes, and mustard growing [21-22]. Initial research on the use of zeolites in agriculture took place in the 1960s in Japan. Japanese farmers have used zeolite rock over years to control the moisture content and to increase the pH of acidic volcanic soils [12]. Modern researchers have noted

the high efficiency of using zeolite and peat-zeolite substrates in the grapes, greenhouse crops, and buckwheat cultivation [23-26]. In addition to natural mineral ores, waste from various industries can be used as agro-fertilizers. The phosphorus extraction in the form of vivianite from wastewater is the starting point for new technologies for the production of phosphate fertilizers [27-28]. The use of waste from processing potash and magnesium ores in cultivation allowed to increase the yield of cereals and potatoes [29]. Microelement additives based on waste from ore processing in the mining and processing industry were used in the cultivation of oats, potatoes, radishes and peas [30, 31].

The composition of some industrial wastes includes molybdenum. Thus, non-ferrous and ferrous metallurgy waste may contain 0.2-0.6% molybdenum, and electric lamp plant waste may contain 5-6% [32-34]. Waste from the Dzhdinsky tungsten-molybdenum combine - Kholoson's adit drains contain 0.475 mg/dm³ of Mo(VI) ions [35], exceeding the standard values by almost 2 times [36].

Therefore, the purpose of this work was to study the possibility of obtaining a non-traditional molybdenum-containing fertilizer based on zeolite tuff.

In this connection, the following tasks were highlighted:

- extraction of molybdenum from molybdenum-containing solutions by zeolite tuffs;
- possibility of using the obtained molybdenum-containing raw materials as a microelement fertilizer.

2 Materials and Methods

Molybdenum-containing non-traditional fertilizer was obtained in the laboratory. Zeolite-containing tuff of the Kholinsky deposit (Transbaikalia) was used as a sorbent. A particle size of 1–2 mm was used. The optimal particle size was obtained as a result of previous experiments [37-39]. The granulometric composition of fertilizer refers to the physical and mechanical properties of fertilizers. The granulometric composition characterizes the flowability and uniformity of fertilizer application over the field area, and affects the soil structure.

The sorption properties of zeolite-containing tuff with respect to molybdenum are characterized by absorption capacity. Solutions of sodium molybdate (Na₂MoO₄) with concentrations from 0.01 mg/sm to 13 mg/sm were prepared. The solutions were filled with suspended zeolite-containing tuff in various ratios of solid phase and liquid (S:L) 1:1; 1:5 and 1:10. The sorption process was carried out in static mode with periodic shaking; duration-1 day (24 hours); T° = 20-25 C°.

Testing of molybdenum-containing zeolite additives was carried out in the conditions of a greenhouse experiment.

Experiments were carried out on chestnut powdery carbonate soil. Such soils make up the main arable Fund of the Republic of Buryatia. Chestnut powdery carbonate soil is characterized by a light-loamy granulometric composition, slightly alkaline reaction of the medium, low humus content, very low availability of nitrate nitrogen and potassium exchange, and medium availability of mobile phosphorus.

The scheme of the experiment provides for the study of the influence of molybdenum-containing zeolite tuffs (MZ) together with mineral fertilizers (table. 2) on the yield of pea plants. The concentration of Mo⁶⁺ ions in the solid phase of zeolite-containing tuff was taken as the basis for the choice of dosages. Leguminous are the most demanding for molybdenum fertilizers. In this regard, peas were chosen as the experimental crop. Peas of the "Sakharny" variety (*pisum sativum* 'saharniy') were planted in vegetation vessels with a capacity of 8 kg. The repetition of options is sixfold. Ammonium nitrate, double superphosphate, and potassium sulphate were used as mineral fertilizers.

Table 2. Scheme of the experiment

№ option's	Experience option	Convention
I	Background – N _{2,9} P _{2,3} K _{2,0} *	B
II	Control – Background + zeolite 10 g/vessel	C
III	Background + MZ (0.5 mg Mo ⁶⁺) 10 g/vessel	MZ _{0.5}
IV	Background + MZ (1.0 mg Mo ⁶⁺) 10 g/vessel	MZ _{1.0}
V	Background + MZ (1.5 mg Mo ⁶⁺) 10 g/vessel	MZ _{1.5}

*N – nitrogen, P – phosphorus, K – potassium; dosage – g / vessel

The chemical composition of the original zeolite-containing tuffs and those used in the greenhouse experiment is presented in Table 3.

Table 3. Chemical composition of the zeolite-containing tuffs of the Kholinsky deposit.*

Index	Units	Content	
		Z	MZ
pH	units	7.8	6.85
SiO ₂	%	68	67.00
TiO ₂		0.09	0.11
K ₂ O		4.52	4.42
Na ₂ O		1.27	1.55
Al ₂ O ₃		12.55	12.60
MgO		0.49	0.51
CaO		1.69	1.54
P ₂ O ₅		<0.05	<0.05
Fe ₂ O ₃		1.00	1.32
MnO		0.10	0.07
Zn	ppm	37	37
Pb		11	18
Mo		75	120
Rb		196	184
Sr		49	44
Y		16	12
Zr		150	139
Nb		24	22
Sn		3	3
Cs		9	11
Ba		112	103
La		30	34
Ce		30	34

*Z -initial zeolite-containing tuffs; MZ - zeolite tuffs modified in a solution of sodium molybdate (Na₂MoO₄)

The accounting of pea's herbage was carried out on 40-th day after emergence by vessels weighing.

The chemical composition of Na₂MoO₄ aqueous solutions was analyzed using quantitative chemical analysis methods. Analyzes were conducted in the laboratories of the "Hydrogeology and Geoecology" and the Shared Research Center "Analytical center of

mineralogical and geochemical and isotopic research of GIN SB RAS" (Russia, Ulan-Ude) by the ISP AES method on an OPTIMA 2000 DV. The chemical composition of zeolite-containing tuffs was carried out by the spectrophotometric method on a UNICO 1201 and by the XRD method on an EDPRS-1 energy dispersive X-ray spectrometer.

3 Results and Discussion

The ion-exchange properties of zeolites are characterized by their ability to absorb ions. The zeolite-containing tuff of the Kholinsky deposit, used as a sorbent, found a sufficiently high capacity for molybdenum (IV). The inflection of isotherm's line of the sorption begins at a point (4.28 mg / cm³; 1.38 mg-EQ/g). The maximum capacity was 1.98 mg-eq/g at a concentration of the initial solution of 13.2 mg/cm³. (Fig. 1)

Fig. 1. Isotherm of Mo(6+) sorption by zeolite tuffs of the Holinskoye deposit

When choosing the optimal T:L ratios, such a factor as cost-effectiveness was taken into account. For further experiments, a solution of 4.28 mg/cm³ sodium molybdate was used. The maximum absorption of Mo⁶⁺ ions was observed at the ratio of zeolite tuff-Na₂MoO₄ solution 1:1 and amounted to 241 ppm of the sorbent (Fig. 2).

Fig. 2. Effect of the S:L phase ratio on Mo 6+ accumulation in the sorbent phase

The study of molybdenum ion sorption isotherms showed that after reaching the

maximum values, the level of Mo^{6+} accumulation decreases. Almost identical indicators of Mo(VI) content in the solid phase 179 ppm (1:1); 175 (1:5) and 180 (1:10) indicate that a state of equilibrium has been reached. This fact characterizes the sorption capacity of the zeolite-containing tuff of the Kholinsky deposit in relation to Mo^{6+} molybdenum ions at the specified parameters. The choice of the ratio "solid phase: liquid" 1:10 is due to the agrochemical efficiency of using smaller volumes of water for initial chemical solutions.

Vegetation experiments have shown the effectiveness of using molybdenum-containing zeolite tuffs as non-traditional fertilizers when growing pea's herbage. An increase in the yield of pea's herbage by 5.4 % relative to the background variant was noted in the control option (Fig. 3). This fact indicates the responsiveness of peas to the addition of zeolite-containing tuff, as a prolongator of the action of mineral fertilizers.

Fig. 3. Increase in the herbage yield when using a molybdenum-containing zeolite additive, % to Background

In MD_{0.5}, MD_{1.0} and MD_{1.5} options, the yield increase relative to the background variant was 9.6, 9.76, and 9.92%, respectively. The maximum yield was noted in the MD_{1.5} option and amounted to 17.2 g/vessel of pea's dry herbage. The effectiveness of the studied fertilizers on pea plants was visually shown at the starting of plants. Pea plants in the options with the addition of a molybdenum-containing zeolite additive were higher and had a more intense green color than the plants of the background and control options.

4 Conclusions

1. The following main stages in the technology of obtaining a molybdenum-containing additive based on the zeolite tuff of the Kholinsky deposit are highlighted:
 - granulation-screening (selection of fractions with a grain diameter of $1 \div 2$ mm)
 - modification (introduction of molybdenum (VI) ions into the zeolite-containing tuff using the sorption process).

Currently, the authors are conducting research on the extraction of molybdenum using zeolite-containing tuffs from molybdenum-containing wastewaters of mining enterprises.

2. A non-traditional molybdenum-containing fertilizer based on the zeolite tuff of the Kholinsky deposit was obtained by sorption method. This fertilizer has the following characteristics: the grain diameter is $1 \div 2$ mm, the Mo (VI) content is $175 \div 180$ ppm.

3. Preliminary research results obtained in the conditions of vegetation experiment have

shown that molybdenum-containing zeolite tuffs of the Kholinsky Deposit contribute to increasing the yield of pea's herbage. The maximum increase in the yield of pea's herbage was obtained when applying MZ to the soil in doses of Mo 1.5 mg per vessel.

4. The use of molybdenum-containing non-traditional fertilizers based on zeolite tuff is promising in order to increase the productivity of agricultural land.

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