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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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OF THE ACADEMY OF SCIENCES
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named after K. I. Satpayev

ГЕОЛОГИЯ ЖӘНЕ ТЕХНИКАЛЫҚ ҒЫЛЫМДАР СЕРИЯСЫ

♦

СЕРИЯ ГЕОЛОГИИ И ТЕХНИЧЕСКИХ НАУК

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TECHNOLOGY OF SALINE LAND RECLAMATION BY BROWN COAL PRODUCTS

Abstract. Object of research is technology of formulation of physiologically active humic products, methods of aqueous solutions preparation and effectiveness of their impacts on seeds and sprouts of grain and vegetable crops, testing the product in rough soil and climatic conditions of the arid zone of Kazakhstan. Therefore, the purpose of paper is development of technology for formulation of preparation and agromethods of its use in order to increase agricultural crop yields in extreme soil and climatic conditions based on laboratory and field tests, biophysical monitoring, and main technological parameters adjustments.

The results of testing experimental sample of the product formulated according to the developed technology and agromethods on various types of low-productive soils of arid zones of the republic are presented. Optimal concentrations of aqueous solutions of humic product for agricultural crops seeds treatment, optimal technological parameters to prepare seeds for sowing (duration of treatment with humic product, tempering, etc.) have been determined by the method of biotesting: optimal conditions for sowing seeds into soil (substrate moisture content, temperature, salinity) have been determined. Research has been carried out in laboratory conditions in winter and on experimental sites in several farms.

As a result of executed work effectiveness of the product formulated according to the developed technology on low-productive soils with a salinity level of 0.8 2.2% was established. Increase in the yield of grain crops reaches 24.2 - 42.1%, rice 76.2 - 78.6%. and soybean - 34.8%.

Key words: brown coal, sodium humate, biotasting, salinization, ecological stability, extreme factors of the environment.

Introduction. New types of compound materials are required in order to fulfill the State Program of Industrial and Innovative Development of Kazakhstan, as well as to solve many tasks of modern industry and agriculture. Complexity of the structure and availability of different functional groups, amino acids, polysaccharides as a part of humus determine such functions as accumulative, mobility, regulatory, protective, physiological, etc. Such materials include modified humic products. Humate-containing compounds have unique properties, which allow them to expand their field of application especially in saline soils.

Besides, modified humic compounds can act as biologically active substances, sorbents of heavy metal, radioactive elements and organic toxic compounds, i.e. they can incorporate some pesticides, hydrocarbons, phenols, etc. These compositions are also used for purification of natural and waste water, re-cultivation of degraded and dust suppressed contaminated soils.

Humic ingredients of brown coal are non-synthetic substances, non-toxic for human and ecosystem as a whole, which is a positive of their use for various needs.

Kazakhstan has significant reserves of brown coal, which are raw materials for these materials production. Despite the availability of large deposits of brown coal in the Republic and sufficiently developed infrastructure for manufacturing such products, their production is not organized. Therefore,

development and industrial implementation of technology for manufacturing of modified humic products from natural hydrocarbon raw material is a critical task, and establishment of production of such materials contributes to expansion of the Republic's export potential and import substitution.

Scientists from Russia, Ukraine, Uzbekistan, Kyrgyzstan, the USA, Canada, Germany, Poland, etc. are engaged in research of physical, chemical and technological basis of the processes of humate-containing products manufacturing. In Kazakhstan research is carried out at the Institute of Organic Synthesis and Coal Chemistry (Karaganda), in particular, method of coal-alkali reagent production used to stabilize mud fluids has been developed, as well as processes of coal oxidation with nitric acid and modification of humic compounds by synthetic polymers have been studied. In the Research Institute of new chemical technologies and materials at the KazNU named after Al-Farabi work on catalytic liquefaction of brown coal with associated extraction of humic compounds. In the Institute of Chemical Sciences named after A.B. Bekturov the scientific basis of the processes for manufacturing humate-containing compound materials has been developed and process flow chart. Technology for manufacturing humic products from brown coal has been developed by D. A. Kunayev Mining Institute. Representative batch of manufactured product was tested as growth stimulator of various agricultural crops.

Water-supply deficit, arid climate and significant part of saline soils in the structure of topsoil of Kazakhstan are serious obstacle for increasing productivity of the land by classical methods.

Non-traditional methodological approaches on using lands having low productivity and increasing in agricultural production which are based on fundamentally new scientific and theoretical concept of energoinformational farming have been developed. Rational use of physiologically active humic products in the fields - adaptogens with multifunctional properties, increasing bioenergetics and ecological stability of agricultural crops to extreme environmental factors will ensure higher yields of marketable products with minimal dependence on unfavorable soil and climatic conditions.

The plant growth stimulant will become competitive in the domestic and foreign markets due to its low price, environmental cleanliness, availability and efficiency. In addition, during manufacturing humic product cheap local raw materials and available reagents are used, its manufacturing is based on usage of standard equipment. Possibilities of export and import substitution of this product are high, because currently, the Republic purchases similar products abroad. Production arrangement according to technology, which is developed on the basis of presented research, will allow not only to replace analogues imported to Kazakhstan, but also to export humic product, as import analogues are inferior in properties and price.

Methods of research. Laboratory experiments were carried out according to B.P. Stroganova's [1] methodology. Seeds of rice, wheat, barley, etc. in the glasses with capacity of 0.5l exposed to scientific scrutiny, they were coached in thermostat in 5-fold replication on highly saline and non-saline cultivation soil according to GOST.

The samples of the following soils were used as cultivation soil: meadow-sierozem irrigated saline soil; takyr-like soil, alkaline and saline soil; takyr-like middle loamy soils. These samples were dried to an air-dry state and bolted (sieve - 3 mm).

Pre-treatment of seeds of rice, wheat and barley was carried out by 0.1; 0.5; 1.0; 2.0; 2.5; 3.0, 3.5; 4.0% aqueous solution of sodium humate for 60 minutes.

Vessels with rice seeds were watered by weight with tap water until cultivation soil was completely saturated. The moisture content of cultivation soil in the vessels with the rest of crops was maintained at the rate of 65-70% out of its total moisture content capacity. Each 100 grams of rice, wheat and barley seeds were soaked for 10,30,60,120,180,240 and 420 minutes. Treated seeds were dried at the temperature of 20-40°C until air-dry condition. Soil salinity levels were determined according to the classifications of N.I. Bazilevich and Ye.I. Pankova [2].

In the vegetation phase of the 1-2, 2-3, 3-4 leaves, rice was fertilized with ammonium sulfate at the rate of 20 kg / ha per each vessel.

Soil moisture content was determined by thermostatically-weighted method using the VPGR-1neutron moisture indicator.

Chemical analyzes of soils were carried out in the chemical laboratories of the Kazgiprovodkhoz Institute, Institute of Soil Science of the Ministry of Agriculture and KazNU named after Al-Farabi.

Technology of humates manufacturing. Ability of humic acids to form salts with monovalent cations of sodium, potassium, and ammonium is the basis of humates extraction from natural raw materials. In order to do this aqueous solutions of the hydroxides of these elements are used. Treatment of carbon-containing raw materials with alkaline reagents leads to disruption of intermolecular interaction and rupture of chemical bonds in macromolecules of organic compounds of coal.

Humates extraction method using the so-called "dry method" technology is known, which is to mix brown coal with 42-45% aqueous solution of sodium hydroxide at a ratio of solid to liquid ratio = 5: 1.

In order to increase the yield of humic acids from coal up to 72-73%, the author has developed a method of electrolytic oxidation of coal on nickel anode during 5-6 hours at the temperature of 60-65 °C. Humic compounds extraction method by oxidizing coals with solutions of nitric acid with concentration up to 40% at the temperature of 75 °C during 3 hours is known. The yield of humic compounds reaches 60-70%.

In order to extract humic compounds, it is known to use chlorine, ozonized air, ozone, nitrogen oxides.

Not only physical-chemical and chemical methods of extraction are being developed, but also physical methods of impact on raw materials: infrasound, radiolysis, baroforming, etc.

Analysis of the known methods [3-7] of humic compounds extraction shows that the most effective and widespread method is the "leaching" of humic substances from fossil raw materials by alkaline solutions.

Research of influence of hydroxides nature, temperature and exit concentration of humates was carried out using LiOH solutions at the concentration from 1 to 10 mol/kg, NaOH and KOH. Ammonia-water mixture was not investigated, due to its non-technological nature (escape of gaseous ammonia) and formation of unstable humates. The results of the research are shown in figure 1.

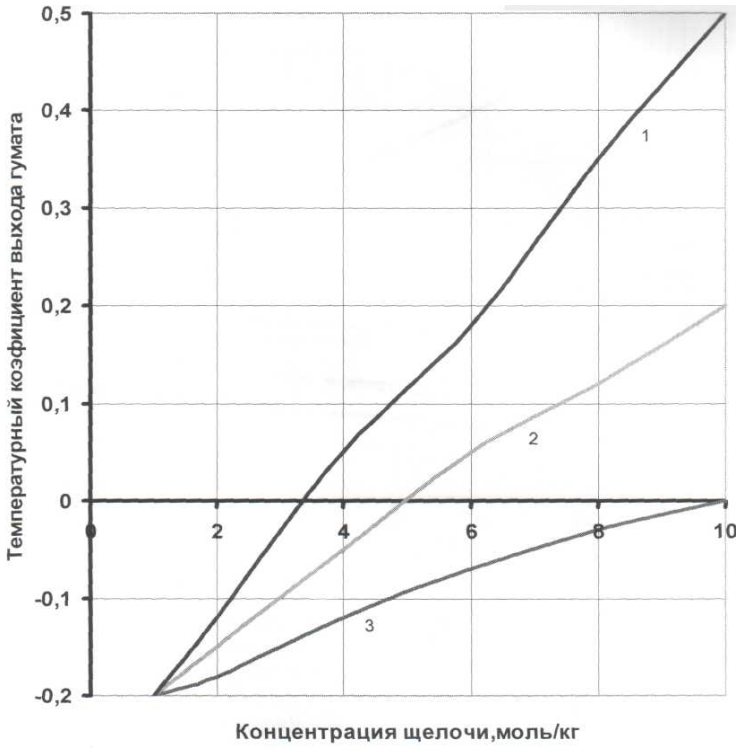

Figure 1 – Temperature coefficient of humates yield as a function of alkali nature and concentration:
1 – LiOH, 2 – NaOH, 3 – KOH '

Specified dependence shows that the highest humates yield up to 90% is observed in LiOH solutions in studied concentrations, and in the solutions of sodium hydroxide it is up to 70%. The activity of hydroxides impact on humates yield shows that the increase is observed in the series LiOH> NaOH KOH. For comparison, in figure 2 dependence of the humate yield during heating of initial coal (curve 5) is

shown. Humates yield reaches 15% during heating the coal up to 200-220 ° C, and during exposition of sodium sulfate solution having neutral reaction of medium to carbon, humates yield, even with heating, is very small and does not exceed 10%. Increase in the concentration of alkali contributes to increase in humates yield, while temperature increase at alkali concentrations (NaOH) from 2 to 4 mol/kg of coal does not increase the humates yield (curve 3, 4).

Increase in concentration of NaOH up to 10 mole/kg of coal promotes the yield of humates by more than 50% at the same temperatures [8, 9].

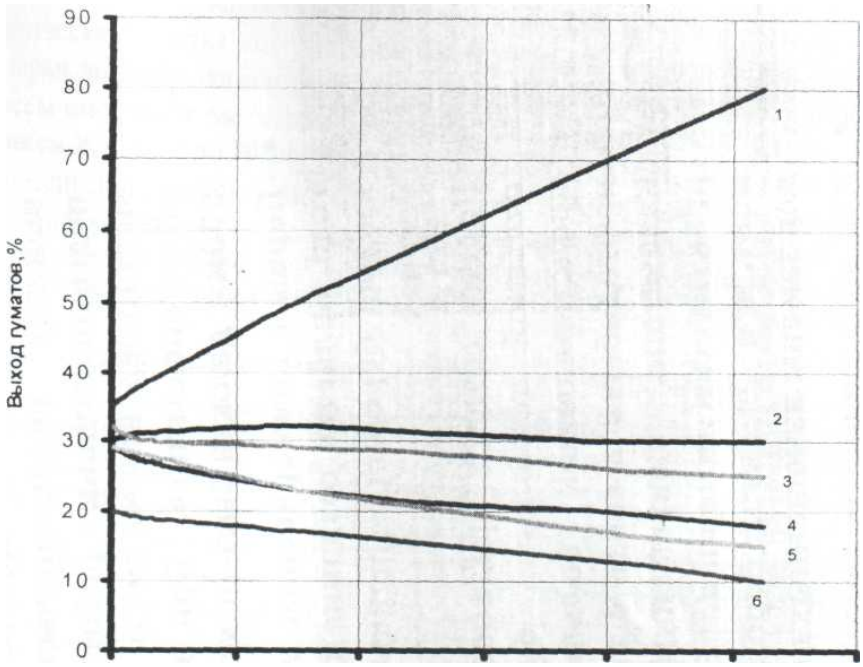

Figure 2 – Temperature dependence of the yield of humates on the nature of solution and its concentration. Temperature degrees C: 1 – system coal-solution NaOH 10 mole/kg; 2 – system coal-solution KOH 4 mole/kg; 3 – system coal-solution NaOH 4 mole/kg; 4 – system coal-solution NaOH 2 mole/kg; 5 – coal (initial); 6 – system coal-solution Na_2SO_4 10 mol/kg.

Reaction of interaction of humic substances with alkali metal ions under normal conditions carries slowly, in practice, extraction of humates is carried out, as a rule, at elevated temperatures and excess pressure [10]. However, despite the fact that the temperature factor has a significant impact on intensity in relatively narrow range - 80-160 °C, the upper limit is restricted by negative effect of higher temperatures on chemical activity of the humates, and the lower limit reduces the yield of the product and increases duration of the process. This fact is confirmed by the results of research by thermography method. These indicators have been the basis of all known technologies.

From the analysis of known methods it follows that currently none of the technologies of humates production has been carried to industrial manufacturing due to objective reasons. The basic requirements to source raw material have not been worked out, solid-to-liquid ratio, concentration of e alkali solution, fractional composition of raw materials and duration of its alkali treatment, temperature regime, etc. have not been accurately determined. Variety of raw materials, because coals not only from different fields differ in composition, but within single field there is considerable range of indicators. Table 1 shows the indicators of composition of brown coal samples from the Kiyakty and Oy-Karagay fields.

Based on the specified data, raw material for humic product manufacturing is extremely heterogeneous, as well as there is significant variation in content of such components as silicon oxide, aluminum trihydrate and ferrum hydroxides, as well as microelements.

These data confirms also variety of technologies, process parameters.

Suggested process is conducted in the following manner: source raw material (brown coal) is purified from foreign impurities by the system of sieves and screens.

Table 1 – Chemical composition of brown coal sample of 2 fields

Indicators	Kiyakty field (medium)	Oy-Karagay field	
		oxide	semi-oxidized
PH of water extract	6,8	6,0	4,7-5,9
Humus, %	20-69,2	30,0	64-72
silicon oxide (SiO2)	38,2-5,0	25,5	25,5
Al2 O3, %	20,5-4,0	21,6	21,6
Fe2O3, %	21-5,2	20,4	20,4
TiO2, %	–	1,25	1,3
MgO	3,2-2,0	1,6	1,6
P2O5, %	0,03-0,05	0,08	0,08
K2O	1,7-2,0	0,75	0,75
CaO	8,3-7,0	17,03	17,03
Na2O	3,1-2,5	0,16	0,16
Nitrogen	0,9-0,8	0,6	0,6
Zink, mg/kg	122-120	1,13	0,16
Cobalt	0,3-0,1	0,19	0,06
Copper	64-60	2,5	0,08
Manganese	20-18	5,4	1,5
Molybdenum	17,0-13	0,25	0,1
Plumbum	104,4-101,0	>32,0	
Cadmium	4,1-3,1	>2,0	

Basically, the process of humates production stipulates following operations; mechanical purification of source raw material from foreign impurities, grinding source raw material to necessary fracture with simultaneous drying. Treatment of obtaining mass with alkali solution at the concentration from 1 to 10% during 2-10 hours and liquid to solid ratio from 5 to 10, at the temperature of 60-80°C, filtration with washing, drying, grinding, screening, packing.

Prepared coal with grain size of not more than 0-5 mm of 0-5 is treated with sodium hydroxide solution at the drum in the rate of 0.4 liter per 1 kg of coal. After determination of concentration tanks with alkali hermetically sealed and left for 12-15 hours. Then accepted stock is unloaded on specially prepared site and is formed into layers of 2-3 cm and dried on air till moistness reaches 18-22%. Optimal parameters were set as a result of tests.

Table 2 – Optimization of process parameters of sodium humate production

Experimental conditions: t - 20-300C, concentration - NaOH - 40%			
Granulometric composition, mm	Ratio: S: L	Leaching time,hour	Humate output
0-2	1:0,5	2 5 10 15	30 40 50 60
0-5	1:0,75	2 5 10 15	40 60 78 85
0-10	1:1	2 5 10 15	30 45 60 70

Produced sodium humate is enriched with solutions of macroelement salts (zinc, molybdenum, cobalt, copper) and macroelements (iron, potassium, phosphorus, nitrogen) with varying concentrations within the following limits (%):

- zinc - 0.10-0.30; iron - 0.10-0.30; molybdenum - 0.05-0.21; cobalt - 0.01-0.06; copper - 0.01-0.06; potassium - 0,03-0,15; phosphorus - 0,03-0,15 (concentrations of micro-impurities were changed depending on their content in source raw material, soil and plant needs).

In order to increase impact of the product on seeds of agricultural plants and increase resistance of sprouts to experimental environmental factors, sodium humate was treated with extract of white-ground Artemisia in the amount of 1-3% out of humate weight.

Artemisia extract was prepared by digestion of dried Artemisia in soft water at the temperature of 20 °C during 12 hours. Use of Artemisia extract is not accidental, since during soaking in 12.5-15% of aqueous extracts of halophytes having physiologically active properties, salt resistance and productivity of cultivated plants are prominently increased. The authors found that this species of Artemisia has a good insecticidal, bactericidal, fungicidal effect, favorably differs from many halophytes.

Therefore, we use optimal concentrations of water extracts of Artemisia white applied during seeds pre-treatment for additional enrichment of new physiologically active humic product in order to improve its multifunctional properties on saline soils.

We checked obtained results on seeds pre-treatment in combination with other agricultural methods which promote accelerated sprouting of rice and crops accompanying rice on saline soils.

It is known that cultivated plants are sensible to adverse effects of salts mostly at a young age, especially during the period of seeds germination and emergence of seedlings. Therefore, obtaining normal sprouts and ensuring their growth and development in the early stages of ontogenesis is crucial for increasing effective fertility of saline soils, and all agronomic measures aimed at accelerating emergence of seedlings contribute to accelerating the growth of plants and their environmental sustainability. One of such measure is creation and maintenance of optimal moisture content of saline soils.

In accordance with biological characteristics, rice seeds on non-saline soils germinate more simultaneously at moisture levels favorable for upland crops. But on saline soils, rice sprouts often die because of excess of salts in the soil solution and impact of alkalizing factors. Therefore, in this case, obtainment and maintenance of seedlings depends primarily on properly selected irrigation mode in the period from seeds chitting to growing plant onto the surface and forming 2-3 leaves.

Study of optimal moisture content of highly saline soil for rice, barley, sorghum and maize seeds treated before dropping in optimal modes with aqueous solutions of sodium humate has been performed under laboratory conditions, the results of which are presented in Table 1. The best medium during germination of sodium humate-treated seeds and during 2-3 leaves stage for both upland crops and rice is moistened cultivated soil substrate (table 2). Moistening levels of highly saline cultivated soil in the range of 60-80% out of the total moisture capacity stimulated germination of the treated seeds and early development of barley, and in the range of 70-90% were most preferable for rice. It is very significant that decrease in the moisture content of highly saline substrate from 70 to 40% contributes to sharp decrease in germination of seeds of the tested crops and causes pronounced pathological symptoms of seedling inhibition, while excessive moistening of cultivated soil less affects early development of plants, but significantly worsens germination of the seeds. Optimal moisture values of highly saline cultivated soil were higher than moisture levels of non-saline soils.

These data suggest that in order to obtain comprehensive sprouts of upland crops to be tested on highly saline alkaline soils of Akdalinsk irrigation tract humidity of upper root layer shall not fall below 70% out of its maximum water holding capacity [11-13].

In the above-described laboratory experiments, levels of salinity and salt compositions of cultivated soils to be tested were constant that allowed establishing stable stimulatory effect of physiologically active humic product on environmental sustainability of agricultural crops under optimal conditions of pre-treatment. Therefore, in further experiments it was necessary to study the impact of different salinity of takyr-like soil on germination of rice seeds treated with sodium humate and plant development in ontogenesis and their seed productivity.

General biological effect of inhibition of plant growth by high concentrations of salts in the soil is known. According to cytological studies of L.D. Avilova [12] the reason of growth inhibition in seedlings

under salt excess is that under these conditions both stages of growth processes of division and cell elongation are inhibited, wherein the second of these stages is inhibited to even greater extent than the first. The nature of growth processes inhibition and size of harvest depend on the type and degree of soil salinity and is determined by the level of biological salt tolerance of cultivated crops in varietal aspect. Therefore it is quite natural and understandable that under various types of salinity seed germination and growth of vegetative organs of rice significantly inhibited, and the higher the level of soil salinity, the stronger inhibition.

Figure 3 – Performance of laboratory experiments on climate chamber

Effectiveness of new physiologically active humic product enriched with micro- and macroelements and wilding plant extracts, e.g. Artemisia white was studied during two laboratory experiments by biotesting. The test was carried out in a mini-climate chamber, manufactured by the staff of D.A. Kunayev Mining Institute 7

Mini climate chamber, according to requirements and GOST (GOST 10250-80 and GOST 12038-84) is equipped light heating devices, timer and thermostats [14-20].

Discussion. Technology primarily involves the following operations: raw materials are mechanically cleaned from foreign materials, crushing the primary raw material to the required fraction, and it is dried. Treatment, washing, drying, crushing, screening of the resulting mass from 2 to 10 hours with an alkaline concentration of from 1 to 10% and from 5 to 10% at a temperature of 60-800 ° C at a ratio of C: K (5:1). All this is explained by the diversity of primary raw materials, as it differs by coal content from different fields, and there is a significant scattering within one field. The brown coal and its bicarbonate are passed through different sieves and put into a vibration mill (molni). It is mixed with 10% aqueous ammonia and is passed to C: K (5: 1), vibration mills, where the coal is 2-6 mm. The bucket produced by this method is divided into trays. It emits carbon dioxide under the influence of the infrared radiator (15-20 Hz) for 5 minute then drops into the tray and dries at 60 ° C for 30 minutes at the time.

Conclusions. The tests of agronomic practice of seeds pre-treatment with humic product allowed revealing its high efficiency at low productive soils and rice plantations of Kyzylorda and Almaty oblasts represented by alluvial-meadow solonchak medium saline middle loamy irrigated soils. I pre-treatment of rice seeds with aqueous solution of the product allowed increasing the yield of rice by 41%. At low productive takyr-like soils of Almaty region efficiency of rice seeds treated with study product rice has increased on non-saline soils by 26.7%, on slightly saline - 37.5% and on highly saline soils -78.6%. It has been established that on brown solonchak middle loamy irrigated soils of Zhezdinsk irrigation tract yield increase in herbage of maize, as well as sorghum and Sudan grass due to seeds pre- treatment with humic product was equal to 22.4 -25.3% and grain - by 30.7% in comparison with control group, where non-treated seeds were used.

Therefore, use of humic product on low productive soils in sub-mountain desert-steppe and desert zones of Kazakhstan provides stable increase in the yield and quality of the target grain and grain legumes products by 20-70% in comparison with the control group. Physiological effect of the product was most effectively manifested during negative impact of extreme factors directly on plants or on their habitats,

which confirms its adaptogenic properties. The product increases bioenergetics of seeds and plants in ontogenesis and changes the quality of interaction between agricultural crops and environment. Physiological activity and adaptogenic properties of the product depend on soil-amelioration conditions of varietal and biological features of crops.

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ҚОҢЫР КӨМІРДЕН АЛЫНҒАН ПРЕПАРАТПЕН ТҰЗДЫ ТОПЫРАҚТА ӨНІМ АЛУ ТЕХНОЛОГИЯСЫ

Аннотация. Мақалада сөз болып отырған зерттеунысаны ол – қоңыр көмірден физиологиялық активті гуминдік препарат алу технологиясы және оны Қазақстанның құнарсыз топырағымен климаттық жағдайында тексеріп көру. Сондықтан біздің мақсатымыз көмір майдасынан препарат алып оны толыққанды ауылшаруашылық өнімін мол алудың жолына далалық-эксперимент және биофизикалық мониторинг арқылы бұл технологияға өзгерістер енгізіп, тиімді параметрлерін анықтау. Сондықтан эксперимент ретінде алынған

препаратты жылма-жыл өнімді аз беретін топырақ жағдайында тексеріп көру. Ол үшін гуминдік препараттың суда еритін және 1 га жерге оның қанша жұмсалатынын есептеп шығардық, оның ішінде бидайдың тұқымын сол ерітіндіге бұқтырып, кептіріп сонан кейін ғана топыраққа себудің режимін анықтадық. Осындай тәжірибелерден кейін анықтағанымыз, топырақтағы тұздың өлемі 0.8-2.2 %-те болғанымен сол жағдайдың өзінде дәнді дақылдан 24,2-42,1 %-ке, күріш 76,2-78.6 %-ке, ал соя - 34,8 %-ке өсім берді. Бұл тұзды топырақтың және құрғақшылығы жиі кездесетін жағдайда көңіл көншітетін көрсеткіш болып есептеледі.

Түйін сөздер: қоңыр көмір, натрий гуматы, биотестілеу, тұздану, экологиялық тұрақтылық, қоршаған орта тұрақсыздығы.

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ТЕХНОЛОГИЯ ОСВОЕНИЯ ЗАСОЛЕННЫХ ЗЕМЕЛЬ С ИСПОЛЬЗОВАНИЕМ ПРЕПАРАТОВ ИЗ БУРОГО УГЛЯ

Аннотация. Объектом исследований являются технология получения физиологически активных гуминовых препаратов, способы подготовки водных растворов и эффективность их воздействий на семена и проростки зерновых и овощных культур, испытания препарата в жестких почвенно-климатических условиях аридной зоны Казахстана. Поэтому цель работы-разработка технологии получения препарата и агроприемов его использования для повышения урожайности сельскохозяйственных культур в экстремальных почвенно-климатических условиях на основе данных лабораторных и полевых испытаний, биофизического мониторинга, а также корректировки основных технологических параметров.

Представлены результаты испытаний экспериментального образца препарата, получаемого по разработанной технологии и агроприемов на различных типах низкопродуктивных почв засушливых зон республики. Методом биотестирования определены оптимальные концентрации водных растворов гуминового препарата для обработки семян сельскохозяйственных культур, оптимальные технологические параметры подготовки семян к посеву (продолжительность обработки гуминовым препаратом, отлежки семян и др.): определены оптимальные условия высева семян в почву (влажность субстрата, температура, засоление). Исследования проводились в лабораторных условиях в зимнее время и на опытных; участках в ряде фермерских хозяйствах. В результате выполненных работ установлена эффективность препарата, получаемою по разработанной технологии на низкопродуктивных почвах с уровнем засоления 0,8 2,2 %. Повышение урожайности зерновых культур достигает 24,2-42,1 %, риса 76,2-78.6 %, а сои - 34,8 %.

Осуществлен монтаж опытной установки по получению гуминового препарата, на которой получено 550 кг препарата. Определены его химические и токсикологические свойства; получен сертификат соответствия КСС № 0049776. Данный препарат был использован при закладке стационарных и производственных испытаниях в хозяйствах Алматинской, Кызылординской и Северо-Казахстанской областях на 5 типах почв. Установлено, что физиологическое действие препарата наиболее эффективно проявляется на силью засоленых почвах в экстремальных почвенно-климатических условиях.

Ключевые слова: бурый уголь, гумат натрия, биотестирование, засоление, экологическая устойчивость, экстремальные факторы среды

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