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TECHNOLOGY OF OBTAINING POLYMER-CONTAINING MICROFERTILIZERS BASED ON COAL WASTE FROM THE LENGER DEPOSIT

Abstract. This article provides information on the development of a technology for the production of polymer-containing microfertilizers based on humic acid obtained by decomposing coal waste from the Lenger deposit. Also describes the composition of coal waste and humic acid determined with using SEM and IR spectrum. For benefication with microelements, a solution of ammophos, boric acid, copper sulfate, potassium sulfate and ammonium molybdenum acidic is added to the mixture obtained, as a chelating agent SAS «GS-1».

The got polymer-containing microfertilizers are characterized by a high content of humic substances, that participate in the structure formation of the soil, accumulation of nourishing elements and microelements in an accessible for plants form, contribute to the regulation of metal content in aquatic and soil ecosystems.

Keywords: polymer-containing microfertilizers, coal waste, humic acid, soil, plants, microelements, chelating agent.

Introduction. Agriculture is one of the key sectors of the economy of Kazakhstan. One of the most important problems of the agricultural industry is increasing soil fertility, which directly affects the increase in crop productivity. For the proper solution of this issue, great importance is the introduction into the soil elements which necessary for the growth and development of plants. These elements are introduced into the soil in the form of organic (manure, peat) and mineral (chemical processing products of mineral raw materials) fertilizers.

Research by scientists and industrialists, as well as laboratory experiments show that industrial waste is a sufficiently valuable secondary raw material for the production of mineral and organic-mineral fertilizers [1].

Coal-mining waste from the Lenger deposit is a promising and valuable source of organo-mineral raw materials and contains a wide variety of trace elements and organic substances with fertilizing properties, and in this regard is a valuable secondary raw material suitable for processing into humic acid [2].

As a result of coal mining in Kazakhstan, more than 6 million tons of waste was generated, and Lenger's deposit of brown coal is located in south Kazakhstan. According to the data, reserve its balance part is 33956 thousand tons, the off-balance part – 3244 thousand tons [3].

The main components of brown coal waste from the Lenger deposit are mineral and organic substances. The mineral part is represented by the constituent components of siliceous, aluminate and calcium compounds. The organic part of brown coal waste is represented by functional groups of organic substances, including humic compounds, in complex with organometallic substances.

SAS «GS-1» – obtained on the basis of gossypol resin by method saponification with the aim of isolation of fatty acids and further esterification with isopropyl alcohol. Widely used in fertilizer manufacturing enterprises as a polymer – chelating agent [4].

EXPERIMENTAL

To obtain a polymer-containing microfertilizer, experimental physicochemical and analytical research methods were selected: electron microscopy, IR spectroscopy, elemental analysis, etc.

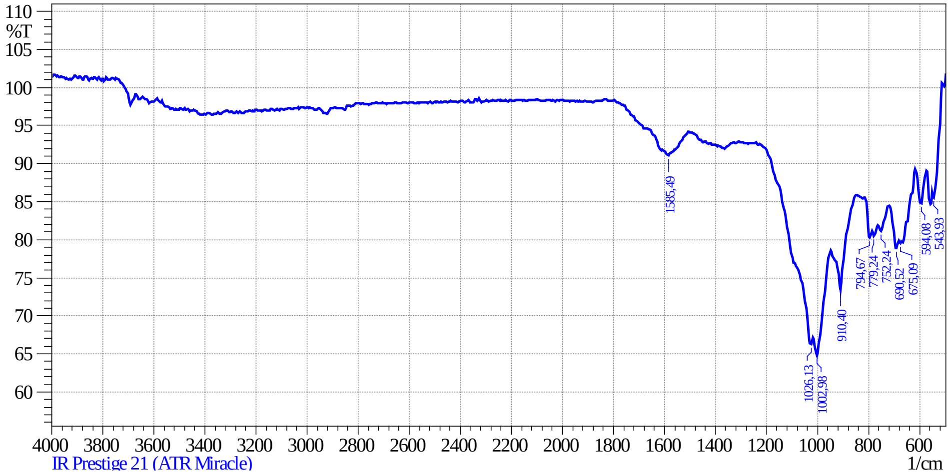

Figure 1 – IR spectrum of coal waste from the Lenger deposit

Figure 1 shows the IR spectrum of coal waste, from which it follows that:

– less intense absorption spectra 1585,5 cm^{-1} characteristic for carboxyl groups with sodium-containing groups –C-ONa;

– absorption spectra with wavelengths 1090-1020 (1033,8) cm^{-1} characterize the presence in coal waste silicate compounds with valence bonds Si-O-Si and Si-O-C, as well as characteristic for oxygen-containing ether groups;

– intense fluctuations in the interval 910,4 cm^{-1}, characteristic of a phosphorus-containing compound and a benzene group C-O-C;

– absorption spectra in the area 794,6–752,2 cm^{-1} characteristic of organic thiophene groups.

Table 1 presents the elemental and mineralogical composition of coal waste.

From the analysis of table 1 it follows that in the elemental composition of the sample waste coal Lenger deposits contains in %: Al – 3,92, Si – 8,06, Fe – 2,09, Mg – 0,30, Ti – 0,26 and etc. Such a content of elements in the composition of brown coal is sufficient to use it as a initial raw materials for the production of humic acids.

Table 1 – The elemental and mineralogical composition of the coal waste from the Lenger deposit

Element	Weight, %	Oxides	In terms of oxides, %
C	42,96	–	–
O	39,66	–	–
Na	0,14	Na_2O	0,19
Mg	0,30	MgO	0,50
Al	3,92	Al_2O_3	7,40
Si	8,06	SiO_2	17,27
S	0,89	SO_3	1,78
K	0,67	K_2O	0,80
Ca	1,05	CaO	1,47
Ti	0,26	TiO_2	0,43
Fe	2,09	Fe_2O_3	2,98

Humates were obtained from brown coal waste from the Lenger deposit by oxidation with a 1% KOH solution (pH medium 12,0). The oxidation process was carried out at the temperature of the reaction mixture 80^0C within 2 hours, moreover, the mass ratio of alkali and crushed coal was 0,125÷0,150:1. To obtain humic acid, humates were precipitated with a 5% hydrochloric acid solution, then filtered in a nutsche filter (pH the filtrate is equal 0,85).

The chemism of this process can be provided as follows:

+ OH > - - COO + - - COO + - - COO (1)

- - COO + - - COO + - - COO + 3HCl > - - COO + - - COO + - - COO + 3Cl (2)

In composition extracted humic acid besides organic compounds also contains mineral substances. To determine the inorganic component, the obtained humic acid was calcined at 500 °C. The elemental composition of the obtained ash content was analyzed by scanning electron microscope. The research results are shown in table 2.

Table 2 – The elemental and mineralogical composition of humic acid

Element	Weight, %	Oxides	In terms of oxides, %
O	38,28	–	–
C	41,80	–	–
Na	0,12	Na_2O	0,16
Al	2,70	Al_2O_3	5,10
Si	4,28	SiO_2	9,17
S	1,51	SO_3	3,02
Cl	4,35	–	–
K	5,40	K_2O	6,50
Fe	1,56	Fe_2O_3	2,23

From the analysis of table 2 it follows that the presence of sulfur up to 1.51% is mandatory for all humic acids, which is confirmed in this case. The absence of phosphorus, the content of which usually reaches to 0.5%, is explained by the fact that coal mining wastes were the initial raw material for the production of humic acid.

As can be seen from the data in figure 2, there are the following IR absorption spectra:

– wide bands of intense vibrations in the intervals 3400–3200 cm^{-1} (3360–3251,8 cm^{-1}), which are respectively characteristic of carboxylic acids with a bound – OH group and methyl, methylene groups;

– intense bands in the intervals 1643,3 cm^{-1}, which are characteristic of organic compounds of the carbonyl group of the aromatic series C(OH)=C-CHO;

– non-intense vibrations in the intervals 1200–1300(1257,5) cm^{-1}, which are characteristic of aromatic aldehydes and an oxygen bridge is formed C-O-C;

– intense vibrations in the intervals 682,80–590,08 cm^{-1}, which are characteristic of organic thiophene groups.

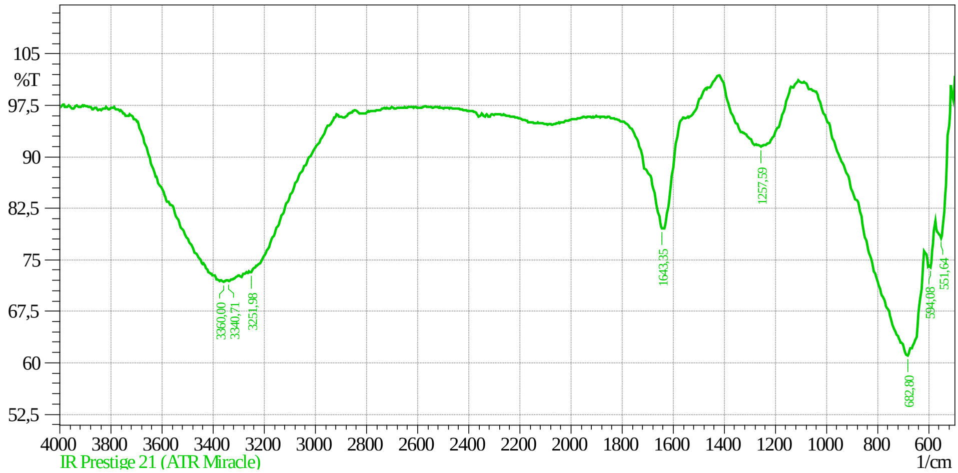

Figure 2 – IR spectrum of humic acid

For carrying out the process of obtaining polymer-containing microfertilizers, including extraction from brown coals of a water-soluble fraction of humic acids, humic acid is used as raw material, the processing of which is carried out by mixing with a 5.0% solution SAS based on gossypol resin by saponification method with the aim of isolating fatty acids and further esterification with isopropyl alcohol (SAS «GS-1»). To increase the total phosphate content in the fertilizer and concentration the finished product with microelements, the resulting mixture is added 5% solution of ammophos and 0.5% boric acid, 0.2% copper sulfate, 1% potassium sulfate, 0.5% ammonium molybdenum. The resulting mixture is thermostated at a temperature of 70°C within 60 minutes. The result is a liquid chelated fertilizer with a pH medium 7.5.

Chemical composition of chelated polymer-containing fertilizer: K_2O – 16,27; ZnO – 1,68; Na_2O – 23,6; MgO – 1,7; Al_2O_3 – 11,3; SiO_2 – 2,66; MnO – 1,20; Fe_2O_3 – 3,75; CaO – 1,28; SO_3 – 10,15; P_2O_5 – 27,8.

Conclusion. The obtained chelated polymer-containing microfertilizer based on brown coal from the Lenger deposit with use SAS «GS-1» as a chelating agent, it gives the necessary microelements to plants for their development.

Application solution SAS «GS-1», received fertilizer concentrated by microelements, which necessary to increase productivity agricultural crops. In addition, in the fertilizer SAS «GS-1» solution plays the role of a chelating agent due to the content of carboxyl groups of fatty acids. The presence of a chelating agent SAS «GS-1» – increases the comprehensibility microelements by plants.

Polymer-containing micronutrient fertilizers are characterized by a high content of humic substances, which participate in the structure formation of the soil layer located around the seeds, the accumulation of nutrients and micro-elements in a form accessible to plants, and contribute to the regulation of the geochemical fluxes of metals in aquatic and soil ecosystems.

The proposed technical solution allows to obtain a chelated polymer-containing micronutrient fertilizer with the necessary content of total, assimilable and water-soluble phosphates, enriched in potassium and microelements, to utilize industrial wastes, reduce the cost and simplify the process, and minimize the generation of industrial wastes.

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Резюме

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ЛЕҢГІР КӨМІР КЕН ҚАЛДЫҚТАРЫ НЕГІЗІНДЕ
ПОЛИМЕРҚҰРАМДАС МИКРОТЫҢАЙТҚЫШ АЛУДЫҢ ТЕХНОЛОГИЯСЫ

Мақалада Леңгір көмір кен калдығынан алынатын гумин қышқылының негізінде жасалынатын полимерқұрамдас микротыңайтқыш алудың технологиясы жайында ақпараттар келтірілген. Сонымен қатар алынған көмір қалдығымен мен гумин қышқылның химиялық құрамына РЭМ және ИК-спектр көмегімен жасалынған нәтижелер келтірілген. Алынатын тыңайтқышты байыту мақсатында, қоспаға аммофос ерітіндісі, бор қышқылы, мыс және калий сульфаттары мен аммонийдің молибденқышқылы қосылады да, ал хелат құраушы полимер ретіне органикалық БАЗ «ГС-1» қолданылады.

Алынған полимерқұрамдас микротыңайтқыш құрамында гумин қышқылының мөлшері көбейіп, топырақтағы құрылымдық құралуға қатысып, құрамындағы қоректік элементтермен микроэлементтерді өсімдіктерге беріліп, сулы және жер-топырақ экожүйедегі металдардың құрамын реттеп отырады.

Түйін сөздер: полимерқұрамдас микротыңайтқыш, көмір қалдығы, гумин қышқылы, топырақ, өсімдіктер, микроэлементтер, хелатқұраушы.

Резюме

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ТЕХНОЛОГИЯ ПОЛУЧЕНИЯ ПОЛИМЕРСОДЕРЖАЩИХ МИКРОУДОБРЕНИЙ
НА ОСНОВЕ УГОЛЬНОГО ОТХОДА ИЗ ЛЕНГЕРСКОГО МЕСТОРОЖДЕНИЯ

В статье приведена информация о разработке технологии получения полимерсодержащих микроудобрений на основе гуминовой кислоты, полученной при разложении угольного отхода из Ленгерского месторождения. Также описывается состав угольного отхода и гуминовой кислоты, определенный с помощью РЭМ и ИК-спектра. Для обогащения микроэлементами в полученную смесь добавляют раствор аммофоса, борную кислоту, сульфат меди, сульфат калия и аммония молибденовокислого, а в качестве хелатообразователя ПАВ «ГС-1».

Полученные полимерсодержащие микроудобрения характеризуются высоким содержанием гуминовых веществ, которые участвуют в структурообразовании почвы, накоплении питательных элементов и микроэлементов в доступной для растений форме, способствуют регулированию содержания металлов в водных и почвенных экосистемах.

Ключевые слова: полимерсодержащие микроудобрения, угольные отходы, гуминовая кислота, почва, растения, микроэлементы, хелатообразователь.