RASĀYAN *J. Chem.*
Vol. 16 | No. 1 |428-433| January - March | 2023
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

TECHNOLOGY FOR OBTAINING CHELATED ORGANOMINERAL MICRO-FERTILIZERS BASED ON HUMATE-CONTAINING COMPONENTS

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ABSTRACT

This article provides information on the technology of obtaining chelated organomineral micro fertilizers based on phosphorus and coal production waste to increase crop yields. The obtained chelated organomineral micro-fertilizers are involved in the structure formation of the soil and eliminate the deficiency of nutrients and increase productivity in the cultivation of crops, also aimed at reducing accumulated industrial waste, which in turn allows you to regulate the environmental situation and partially solve the issue of industrial waste disposal.

Keywords: Chelate, Micro Fertilizer, Coal, Humic Acid, Humate, Chelation Agent- EDPAN.

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INTRODUCTION

Chelated fertilizers demonstrate high digestibility of macro-and microelements by plants, which allows several times to reduce the chemical load on the soil. A distinctive feature of the chelating agent is the ability to firmly retain trace element ions in a soluble state until they enter plant cells. Therefore, the use of chelated organomineral micronutrients in the cultivation of agricultural crops is of particular interest and demand among potential entrepreneurs.[1-2] The purpose of the scientific work is to develop a technology for obtaining chelated organomineral micronutrients based on phosphorus and coal production waste to increase the yield of agricultural plants. Also, the technology being developed is aimed at reducing accumulated industrial waste, which in turn makes it possible to improve the environmental situation in the region.[3-4] The developed chelated organomineral micro-fertilizers have high mineralogical, and agrotechnical properties and give plants the necessary minerals for their development during the growing season, and have a positive effect on yield.[5-6]

EXPERIMENTAL

To obtain chelated micro-fertilizers, modern analytical (quantitative and qualitative), thermodynamic, chemical, as well as computational, laboratory, and experimental-industrial methods were selected using a scanning electron microscope (SEM) of the Jeol JSM-6490l V brand, a multiparametric portable cyber scanner (PCD 650 Eutech), an IR Fourier spectrometer (Zhimadzu IR Prestige-21), differential thermal analyzer (DTA) and X-ray energy dispersive microanalyzer INCAEnergy (Oxford Instruments). The process of obtaining potassium humate and humic substances from the Lenger coal waste was carried out under laboratory conditions in accordance with GOST 9517-94. The process of obtaining potassium humate is carried out by continuous mixing at a temperature of 40-80^{0}C for 80-120 minutes. Due to an increase in the concentration of alkali used in the production of potassium humate, the yield of the resulting potassium humate increases.[7] The results of the experimental work are shown in Table-1.

Table-1 shows that at 5% of the alkali concentration and at a temperature of 80 ^{0}C, the yield of potassium humate is 96.67%. During the extraction process, there is no need to further increase the concentration of alkali, since, firstly, the chemical composition of humate is the maximum amount, and secondly, the consumption of alkali required for the process increases.

http://doi.org/10.31788/RJC.2023.1618007

Table-1: Alkali Concentration at the Output of Potassium Humate and Temperature Dependence

Temperature, ^{0}C	The yield of potassium humate in the total amount, %	The concentration of potassium hydroxide, %		
		1	3	5
40		77,35	81,22	91,25
60		79,28	84,98	94,37
80		80,22	87,32	96,67

Chemism of this process can be described in the following way:

$$CW + KOH \rightarrow HA\text{–}COOK \quad (1)$$

Where: CW - coal waste; HA – COOK – potassium humate

The elemental and mineralogical composition of the resulting potassium humate was determined using an electron microscope (JSM-6490l V, Jeol. Japan). The results of the study are shown in Table-2.

Table-2: Elemental and Mineralogical Composition of Potassium Humate

Element	Weight %	Oxides	In terms of oxides, %
C	54,02	-	-
O	23,26	-	-
K	19,41	K_2O	23,4
Na	0,29	Na_2O	0,39
Al	0,62	Al_2O_3	1,17
Si	0,94	SiO_2	2,01
S	0,88	SO_3	2,20
Fe	0,58	Fe_2O_3	0,83

Table-2 shows that in the composition of potassium humate, the content of carbon (C) is 54.02 %, potassium (K) is 19.41%, etc. This content of elements in the composition of potassium humate is sufficient for its use as humate-containing components.[8] It is known that the amount of phosphorus transferred from the cottrel dust into the solution is a phosphorus-containing compound and forms monocalcium phosphate. Table-3 shows the elemental and mineralogical composition of monocalcium phosphate.

Table-3: Elemental and Mineralogical Composition of Monocalcium Phosphate

Element	Mg	Al	P	S	Ca	Na	Fe
mass fraction, %	0,04	0,25	11,45	0,08	8,05	-	0,6

It follows from Table-3 that the phosphorus content in monocalcium phosphate is 11.45%, such a phosphorus content is sufficient to use it as a phosphorus-containing fertilizer. Based on the data in Fig.-1, the formation of a crystal structure in the microstructural image of the formed calcium monophosphate is described. It was determined that the mixture contains calcium, phosphorus, and a small amount of magnesium, iron and aluminum.

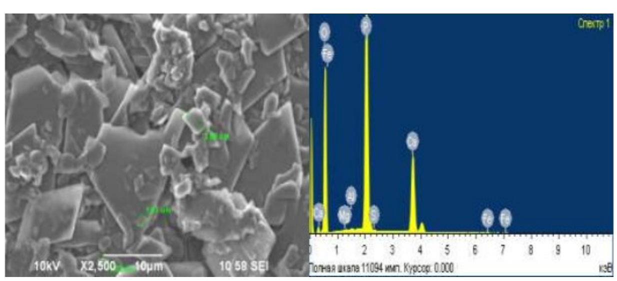

Fig.-1: Microscopic Image of Monocalcium Phosphate

Since monocalcium phosphate was obtained by dissolving it in a solution of sulfuric acid, the hydrogen content in the medium indicated an acidic medium. In the process of mixing monocalcium phosphate with potassium humate, a neutralization reaction occurs to obtain phosphorus-potassium-humate-containing fertilizer at a temperature of 60^{0}C for 60 minutes. We express the equation of formation of the compound as follows:

$$Ca(H_2PO_4)_2 \cdot H_2O + HA\text{–}COOK = (HA\text{-}COO)_2Ca + 2KH_2PO_4 + H_2O \quad (2)$$

To determine the elemental composition of phosphorus-potassium-humate-containing compounds obtained during experimental studies, the sample was dried at 100^0C for 60 minutes, and water was removed, after which the precipitate was examined using electron microscopy (JSM-6490l V, Jeol). The results are shown in Fig.-2 and Table-4.

Table-4: Elemental Composition of Phosphorus-Potassium-Humate-Containing Compounds

Element	Weight %	Oxides	In terms of oxides, %
C	47,21	-	-
O	21,45	-	-
P	11,45	P_2O_5	26,2
K	13,32	K_2O	27,4
Na	0,29	Na_2O	0,39
Al	1,62	Al_2O_3	1,17
Ca	1,23	CaO	1,72
Si	0,94	SiO_2	2,01
S	0,88	SO_3	2,20
Fe	1,61	Fe_2O_3	1,86

Table-4 shows that phosphorus - 11.45%, potassium - 13.32%, iron - 1.86%, and carbon - 47.21%. The presence of useful components in the composition replaces the raw macro- and microelements necessary for the production of phosphorus-potassium-humate-containing compounds. Based on the data in Fig.-2, the presence of phosphorus, potassium, and carbon determines the elemental composition of phosphorus-humate-containing compounds. This mixture is a ready-made raw material for the production of chelated fertilizers.[9]

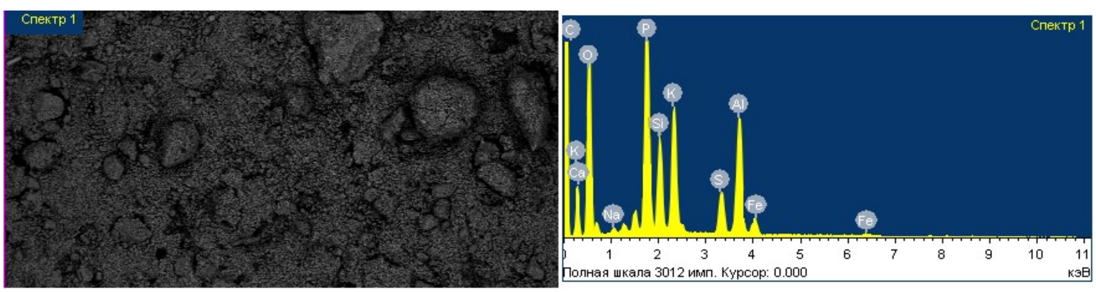

Fig.-2: Microscopic Image of Phosphorus-Humate-Containing Compounds

To obtain chelated micro-fertilizer, the resulting complex mixture containing phosphorus and potassium humate as trace elements is added 0.2% zinc sulfate - 1.5g, 0.5% magnesium sulfate - 2g and the mixture is thermostated at 600C for 60 minutes, then (pH = 4.16) 0.5% etherified derivatives of hydrolyzed polyacrylonitrile (EDPAN) is added. The result is a liquid-chelated micro-fertilizer. To determine the elemental and mineralogical composition of the chelated micro-fertilizer obtained, it was analyzed using electron microscopy (JSM-6490l V, Jeol). The results of the study are shown in Table-5 and Fig.-3.

Table-5: Elemental and Mineralogical Composition of Chelated Micro-Fertilizer

Element	Weight share,%	Oxides	Percentage of oxide in calculation,%
C	43,63	-	-
O	22,71	-	-
P	11,45	P_2O_5	26,21
K	13,32	K_2O	16,05
N	1,31	-	-
Mg	1,79	MgO	2,98
Fe	1,61	Fe_2O_3	2,49

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Zn	1,45	ZnO	2,17
Na	0,29	Na_2O	0,39
Al	0,62	Al_2O_3	1,17
Si	0,64	SiO_2	2,01
Ca	0,51	CaO	2,34
S	0,57	SO_3	2,20

It follows from Table-5 that chelated fertilizers contain the main components, phosphorus 11.45%, potassium - 13.32%, iron - 1.86%, carbon - 47.21%, and the trace element is: iron – 1.61%, zinc - 1.45%, magnesium – 1.79%. Such content of basic and trace elements is sufficient to use chelated fertilizers to eliminate nutrient deficiencies in the soil and increase crop productivity. It follows from Fig.-3 that the presence of an organic polymer etherified derivatives of hydrolyzed polyacrylonitrile (EDPAN) ensures the formation of a granular crystal structure of chelated micro-fertilizers, and the composition of fertilizers depends directly on the composition of the feedstock.

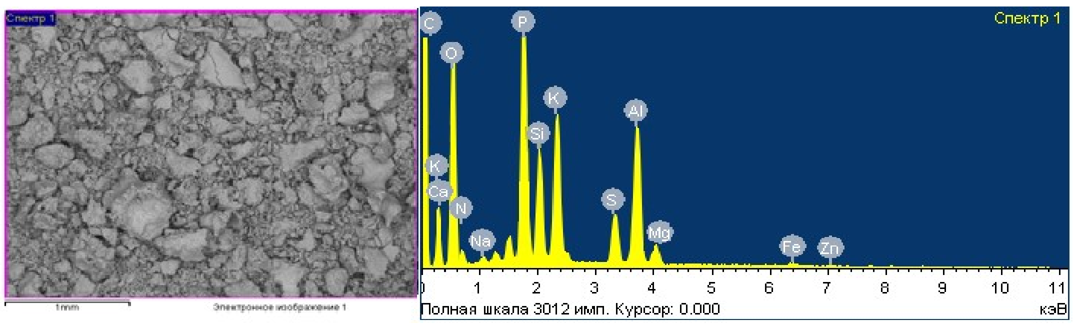

Fig.-3: Microscopic Image of Chelated Micro-Fertilizer

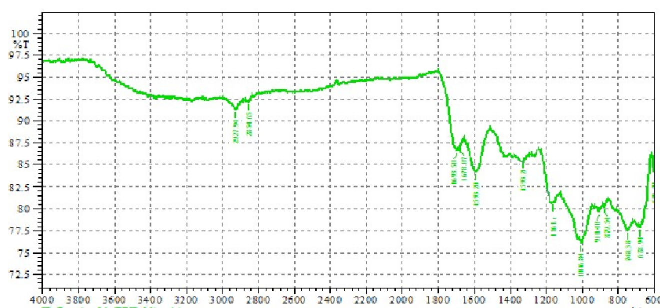

Fig.-4: IR Spectrum of Chelated Micro-Fertilizer

Analyzing the absorption graph of the bands of the IR spectrum of the chelated micro-fertilizer in Fig.-4, it was found that at a value of 1355.0 cm^{-1} in the spectrum, the elements of macro- and microelements in the micro-fertilizer are in the organic chelated form of metals such as iron, magnesium, and zinc. IR spectral analysis of chelated micro-fertilizer revealed the presence of the following organic functional groups:

- less intense absorption spectra in the ranges - 3000-2800 cm^{-1} (2927.91-2854.65) determine the compounds between carboxylic acids - OH groups, methyl groups, and methylene groups;
- intense absorption bands in the intervals of 1700-1500 cm^{-1} (1693,5-1678,07-1593,2) cm^{-1}, defines compounds of carbonyl and aromatic hydrocarbons;
- intense absorption bands in the range of 1355.0 cm^{-1}, characteristic of carbonyl hydrocarbon compounds forming chelated compounds R-C-O-K, (R-C-O) 2-Me, through an oxygen bridge;
- non-intensive absorption of 1161.15 cm^{-1}, characteristic of compounds of aromatic aldehyde hydrocarbons forming the C-O-C oxygen bridge;

- the intense spectral absorption bands in the intervals of 910.40-879.54 cm-1 correspond to organic thiophene compounds and determine which form an oxygen bridge between phosphorus and carbon (P-O-C).
- the intense spectral absorption bands in the ranges 748.38-678.94 cm-1 correspond to organic methylene compounds.

RESULTS AND DISCUSSION

It was determined that the yield of potassium humate at 5% of the alkali concentration is 96.67% at a temperature of 80^0C. The elemental and mineralogical composition of potassium humate obtained according to GOST 9517-94 was determined using an electron microscope (JSM-6490l V, Jeol. Japan). The resulting regression equation makes it possible to determine whether it is possible to achieve a high yield by determining the influence of all factors affecting the process of obtaining potassium humate. According to the results of experimental work on the basis of the method of mathematical planning, it was found that the optimal indicator of the extraction process of potassium humate at a temperature of 80^0C and a time of 120 minutes is 96.71% potassium humate at a potassium concentration of 5% hydroxide solution. Experimental data on the production of monocalcium phosphate and the phosphorus content in it is 11.45%, as well as the elemental composition of the main components, is presented. During the study, the optimal parameters of the process of mixing monocalcium phosphate with potassium humates were determined and the ratio of liquid phases S:L = 1:1 was established, the process temperature was -80^0C, the processing time was -60 minutes and the pH of the medium was 6.8. According to the results of experimental work, it was found that an organic polymer (EDPAN) provides the formation of a granular crystal structure of chelated micro-fertilizers, as evidenced by a microscopic snapshot of fertilizers. The optimal technological parameters of the process of obtaining chelated micro fertilizers and the mineralogical composition of fertilizers have also been determined According to the results of spectral studies, it was revealed that the absorption spectra of trace elements in the intervals of 1355.0 cm^{-1} in the chelated micronutrient are in organic chelated forms, such as iron (Fe), magnesium (Mg), and zinc (Zn).[12,13]

CONCLUSION

A technology for the production of chelated micronutrients based on monocalcium phosphate and potassium humate has been developed. The elemental compositions and mineralogical features of the starting materials have been studied. Optimal parameters of the process of obtaining chelated micro-fertilizer have been determined. The developed technology for the production of chelated micronutrients based on monocalcium phosphate and potassium humate has a high solubility and digestibility of phosphorus and a high content of potassium humate, which are involved in the structure formation of the soil, the accumulation of nutrients and trace elements in an accessible chelated form, contribute to the regulation of geochemical flows of metals in aquatic and soil ecosystems.[10-11] When using chelated mineral fertilizers, the structure of the soil improves, and its buffer and ion-exchange properties of soil microorganisms become more active.[12-14] It is recommended to use chelated micro fertilizers in order to eliminate nutrient deficiencies and increase productivity when growing crops in low-fertile soil, that is, saline soil and climatic conditions of Kazakhstan, it is especially important to note the ability of plants to resist diseases, drought, waterlogging, which was revealed by the results of field tests.[15-16]

ACKNOWLEDGMENTS

The work was carried out at NJSC «South-Kazakhstan university named after M. Auezov» under the program of grant financing for young scientists under the project "Zhas galym" for 2022–2024, implemented by the Committee of Science of the Ministry of the Science and Higher Education of Kazakhstan Republic, under the program AP14972664-Development of technology for obtaining humate-containing fertilizers to increase soil fertility and crop yields.

CONFLICT OF INTERESTS

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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