

STUDY OF THE PROCESS OF OBTAINING ORGANOMINERAL FERTILIZERS BY NITRIC ACID OXIDATION OF COAL OF TAJIKISTAN

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Abstract: The aim of the study is to study the composition of coals from the Fan Yagnob and Shurab deposits, as well as to determine the optimal conditions for the oxidation of these caustobiolites.

To achieve this goal, studies were carried out on the composition of the feedstock: coals from the Fan Yagnob and Shurab deposits of Tajikistan.

It has been established that the brown coals of the Shurab deposit are characterized by a high content of humic acids. The study of the elemental composition of Tajik coals showed the presence of alkali metals in them, such as sodium, potassium, magnesium, as well as the presence of trace elements: manganese, copper.

The effect of technological parameters, such as the concentration of nitric acid, the duration of oxidation, the ratio of initial substances on the yield of humic substances, has been studied. The optimal conditions for the oxidation of coal from the Fan Yagnob and Shurab deposits were: temperature 450C, oxidation time 90 minutes, ratio coal: $\text{HNO}_3 = 1:2$.

Experiments on the study of the kinetics of oxidation of coals from the Shurab and Fan Yagnob deposits showed that during the oxidation of coals for 120 minutes, the yield of humic acids increases.

The elemental composition of the liquid phase after coal oxidation - in the filtrate, as well as the solid phase - coal after oxidation were determined. It has been established that some elements such as: boron, sodium, magnesium partially pass into the liquid phase. Due to this, the amount of some elements in the oxidized coal decreased.

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Introduction

Currently, there is an increased interest in humic substances all over the world, the technologies for their production are being improved, the raw material base is expanding, which involves more and more new types of coals, peat, slates, sapropels and lignins.

Humic substances are complex mixtures of biodegradable high-molecular dark-colored organic compounds of natural origin, formed during the decomposition of plant and animal residues under the action of microorganisms and abiotic environmental factors. Humic substances are a macrocomponent of the organic matter of soil and water ecosystems, as well as solid fossil fuels. The generally accepted classification of humic substances [1, 2] is based on the difference in solubility in acids and alkalis. According to this classification, humic substances are divided into three components: humin is a non-removable residue, insoluble in either alkalis or acids; humic acids - fraction of humic substances, soluble in alkalis and insoluble in acids (at pH <2); fulvic acids - a fraction of humic substances, soluble in both alkalis and acids [4]. Both of these acids are the most mobile and reactive component of humic substances, actively participating in chemical processes in ecosystems [1]. As a generic name for both humic and fulvic acids, the term "humic acids" is used [4].

Usually, during the extraction of humic acids from peat and brown coal, a larger amount of the substance is dissolved in alkali than is subsequently precipitated during acid treatment; the organomineral substances remaining in the solution are nothing but fulvic acids. Concentrated solutions of sodium, potassium and ammonium humates are obtained by processing the studied samples of coal with 1% solutions of caustic soda and caustic potash and 5% ammonia water (ratio S:W=1:10). Humic acids are precipitated from them with a 5-10% hydrochloric acid solution at room temperature and pH 1-2. Solid preparations can be obtained by treating coal with concentrated alkali, the consumption of which is calculated based on the yield of humic acids. Considering that a small excess of alkali is required, we can recommend the following consumption of alkali per 1 kg of organic mass of coal: with a content of humic acids of 25% - 75 g, 50% - 150 g, and at 100% (which is quite possible for a number of samples of oxidized brown coals) – 300 g [3; 4].

The yield of humic acids and the content of active functional groups [5;6] are the main indicators that determine the quality of humic preparations.

Soluble humates, as genetic relatives of humus, have biological activity and are used in agriculture as plant and animal growth stimulants. The natural origin and the

absence of traces of humates in the plants treated with them, as well as in the fruits and meat of animals, shows their ecological purity. Humates are non-toxic, non-carcinogenic, non-mutagenic and non-toxic. They are approved for use by both international and domestic organizations. In animal husbandry, humates are used as feed additives when growing young animals (10-15 mg per 1 kg of live weight, solution concentration 0.003%), which leads to an increase in their weight on the same feed by 15-20% and prevents dyspepsia. In crop production, humates are used in the form of 0.005-0.01% solutions. They increase the yield by 15-30%, promote the survival of seedlings during transplantation, increase the germination of seeds, accelerate the ripening of berries, fruits, vegetables, increase the content of proteins, sugars, vitamins and other nutrients in them, reduce the content of nitrates and pesticides in plants, give brighter coloring of flowers, increase the size of inflorescences, prevent late blight disease. Sodium, potassium, and ammonium humates are produced by various companies in the form of solid, liquid, and pasty products [7].

Tajikistan has large reserves of coal, there are about 40 coal deposits. These coals differ both in calorific value and in the amount of humic acids. For the first time, the composition of coals from the Fan Yagnob and Shurab deposits was studied and their suitability for the production of organomineral fertilizers was determined. Taking into account the low content of humus in the soils of Tajikistan, as well as the need for agriculture in organomineral fertilizers, for the first time a technology has been developed for obtaining organomineral fertilizer and plant growth stimulants based on coals from the Fan Yagnob and Shurab deposits. For the first time the technology of complex processing of coals of Tajikistan was developed.

Experimental part

As already noted in the introduction, weathered coals are the best raw material for the production of humic preparations [1]. They contain a greater amount of humic acids, and already the first alkaline treatment converts up to 90% of humic acids from their total content in coal into solution. Extraction can be carried out without boiling the reaction mixture, and the choice of alkaline reagents for extraction is quite wide. This indicates that the technology for obtaining humates from coal weathering can be

relatively simple. Therefore, in most methods for obtaining humates, it is proposed to use weathered coal seams as a raw material. However, despite the high quality of weathered coals as a source of humic preparations and significant reserves, their industrial use causes difficulties. The main reasons for this are the dispersal of occurrence areas and the difficulty of separate extraction, as well as the variability in the quality of raw materials. The content of humic acids in them strongly depends on the degree of oxidation and varies widely.

To organize the industrial production of humic preparations, large concentrated reserves of cheap raw materials of constant quality are needed. Such raw material can be ordinary brown coal, which is mined at the Fan-Yagnob coal deposit and currently amounts to more than 8 million tons per year. They contain 4.1% humic acids per organic mass.

Brown coal can be oxidized with any oxidizing agent. Air, oxygen, ozone, hydrogen peroxide, sulfuric acid, oleum, sulfuric anhydride, Caro's acid, a mixture of nitric and sulfuric acids, nitric acid, nitrogen oxides, chromates, permanganates, halogens, chlorine dioxide, hypochlorites and hypobromites can be used for this purpose. From the point of view of use in large-capacity industrial production, some of them are of interest: air, oxygen, sulfuric and nitric acids, nitrogen oxides.

Most of the oxidizers used in the practice of coal oxidation can be considered acceptable only for scientific purposes, and work with them is only important for studying the chemical composition and structure of fossil fuels and the mechanism of their oxidation. These oxidizing agents include: potassium permanganate, hydrogen peroxide, ozone - its use for the oxidation of coal in an environment of organic solvents [8; 9] and others.

From a practical point of view, nitric acid is the most attractive oxidizing agent for brown coal. It is produced in large quantities at our three nitrogen plants and until recently it was completely processed into ammonium nitrate. But due to the explosive nature of the latter, its production may be reduced, which means that capacities for nitric acid will be released. There is a real opportunity to direct free nitric acid to the

oxidation of Shurab brown coal and, on this basis, to create a large-scale production of organomineral fertilizers.

The so-called oxidative-hydrolytic method for the splitting of brown and black coals with nitric acid has been developed [9].

The essence of this method lies in the use of 12 normal (sp. weight 1.35) nitric acid for the oxidation of coal. To establish the optimal conditions for the oxidation of coals, nitric acid of various concentrations (from 1 to 12 N solutions) was used in the works; coals were treated with it both under pressure in an autoclave and under normal conditions. It was found that when using dilute nitric acid, although a high yield of humic acids is achieved, this product consists of two phases: sediment and solution, which makes it difficult to transport and use in agriculture. When separating the precipitate from the solution, water-soluble organic products are lost.

Humic fertilizers can only be obtained in the solid state by processing coals in the cold (in a porcelain cup or in a glass) with 12 N. nitric acid (monohydrate) in a ratio of 1:0.40. Oxidation proceeds very vigorously with a large release of nitrogen oxides and an increase in the temperature of the reaction mixture to 70-90°C. The output of humic acids reaches 65-70%. The oxidation products are powders even after they have been neutralized with a gaseous or 25% aqueous ammonia solution. They are an amorphous substance, highly soluble in an aqueous solution of alkali.

In [1,9], the products of oxidation of Angren brown coal with a content of 12% humic acids by 56% nitric acid were studied depending on the ratio of coal and nitric acid (monohydrate), (t:l) - 1:1; 1:0.75; 1:0.60; 1:0.40 and 1:0.075. The oxidation conditions for the first four ratios were 10 min. at 95-100°C, for the last ratio - 60 min. at 95-100°C and blowing with oxygen. The yield of humic acids was 81.5% for the ratio (1:0.75), 80.7% for the ratio (1:0.60), 74.0% for the ratio (1:0.40) and ratio (1:0.075) - 30.8%.

In [10], the optimal mode of oxidation of Maykubensky brown coal with an initial content of humic acids not more than 5% (per organic mass of coal) with nitric acid was found: oxidation temperature 75°C, reaction time 180 min, concentration of nitric acid 40%, coal size 3 0-1.0 mm, acid solution consumption, g/g coal, 5:1. The actual yield of

humic acids was 70% on the organic mass of coal. Nothing is said about the loss of nitrogen during oxidation.

In [1,11], the process of oxidation of brown coal from the Angren deposit with nitric acid was studied depending on the acid concentration, temperature, duration, and weight ratio of coal:acid. It has been shown that it is possible to increase the content of humic acids in coal from 4.1% to 57.2% if 40% HNO₃ is oxidized at 40°C for 2 hours at a weight ratio of the organic part of coal to nitric acid monohydrate, equal to 1:2. The loss of nitrogen oxides in the gas phase is 9.2%.

As already noted in the literature review, the most accessible and effective oxidizing agent for brown coal is nitric acid. But when it is used in the process of oxidation, a large amount of nitrogen oxides is released into the gas phase [11].

In [1], the process of oxidation of brown coal from the Angren deposit with nitric acid was studied depending on the acid concentration (10-40%), temperature (30-60°C), duration (25-120 min.) and the weight ratio of coal: acid (from 1 :0.4 to 1:2). It has been shown that it is possible to increase the content of humic acids in coal from 4.1% to 57.2% if 40% HNO₃ is oxidized at 40°C for 2 hours at a weight ratio of the organic part of coal to nitric acid monohydrate equal to 1 :2. But at the same time, if the loss of nitrogen oxides (NO and NO₂) is 9.2% of the organic part of the product obtained. then the process of converting the carbon-containing components of the raw material into humic acids proceeds more efficiently. Therefore, we decided to check these data on the example of coal oxidation in Tajikistan from the Shurab and Fan-Yagnob deposits. In the work, a representative sample of Tajikistan was used, which, after drying to an air-dry state and grinding in a ball mill to a size of 0.55 mm, has the following composition (wt.%): moisture 2.14-11.12; ash 9.05-46.01; organic substances 51.20-81.22; humic acids 0.711-24.01% on organic weight (table 1).

Table 1 gives the chemical composition of the initial coal of the Shurab and Fan-Yagnob deposits and their dumps. Table 1 shows that the ash content and organic mass of coal in the intervals of 70 - 250 m in depth is 9,05 – 16,08 and 76,14 – 81,22%, respectively, and humic acid relative to the organic mass of coal is 19,31 – 24,01%. A

large amount of coal has been accumulated in coal dumps with a mass content of %: ash – 22,01, OMC – 68,04 and HA relative to OMC – 10,74.

Table 1. Chemical composition of initial samples of coals of Tajikistan

№ samp.	Sampling location	Content, mass, %			The output of humic acids on the organic mass of coal, %
		Moisture	Ash	Organic mass of coal	
Shurab field					
1	Mine No. 8, depth 200-250m	10,10	9,05	81,22	19,31
2	Mine No. 8, depth 150m	8,01	16,08	76,14	24,01
3	Mine No. 8, depth 70m	11,12	10,02	79,10	20,73
4	Mine No. 8, surface (dump farm)	10,09	22,01	68,04	10,74
Fan-yagnob field					
5	DP "Mine Fan-yagnob" (eastern flank)	3,07	28,02	69,11	1,043
6	DP "Mine Fan-yagnob" (eastern flank, dump)	3,10	27,13	70,21	1,301
7	LLC TALKO resource (western and central flank)	2,14	22,26	76,08	0,711
8	LLC TALKO resource (western and central flank, dump)	3,09	46,01	51,20	8,157

As tabular data show, the Fan-Yagnob field is of low quality compared to the Shurab field, especially in terms of the relative content of HA.

On the Eastern and western-central flank, the content of HA in the samples is 1,043 and 0,711%. The highest ash content of 46,01% is observed in coal samples from the dumps of the western-central flank, the organic mass in them does not exceed 51,20%.

Table 2 presents the results of the elemental composition of the ash of the initial coal samples of Tajikistan determined by mass spectrometric (ICP - MS) methods of analysis. Table 2 shows that the main constituent elements are: Ca, Mg, Al, Fe, Na and K. Their contents vary in the ranges, wt %: 0,23÷20,01; 0,35÷5,40; 1,7÷7,0; 1,2÷6,4; 0,25÷5,9 and 0,36÷3,30 respectively.

The liquid phase and all washings were collected separately, the total volume was measured, and water-soluble organic matter was determined by evaporating the solution in a water bath and drying the solid residue to constant weight, followed by burning it to determine the ash content and subtract it.

Table 2. Elemental composition of the ash of the initial coal samples of Tajikistan
 (mass spectrometric ICP - MS analysis)

№	Content of elements, mass, %	No. of samples correspond to the numbers table 1							
		1	2	3	4	5	6	7	8
1	B *	0,0027	0,0024	0,0025	0,0016	0,0032	0,0020	0,0018	0,0016
2	Na *	1,6	1,2	1,8	5,9	0,27	0,41	0,26	0,25
3	Mg *	5,4	2,2	3,9	4,5	0,53	0,81	0,40	0,35
4	Al*	3,7	3,0	4,3	4,1	2,3	7,0	3,2	1,7
5	P	0,078	0,10	0,076	0,090	0,13	0,14	0,10	0,097
6	K *	0,40	0,36	0,40	1,6	2,9	3,0	2,7	3,3
7	Ca *	20	10	15	11	0,36	1,0	0,31	0,23
8	Mn	0,088	0,035	0,060	0,68	0,0057	0,026	0,011	0,010
9	Fe*	2,9	6,4	5,3	6,4	1,2	4,2	2,0	1,4
10	Co	0,0013	0,00078	0,0033	0,0014	0,0017	0,0019	0,0032	0,0042
11	Cu	0,012	0,045	0,010	0,014	0,020	0,025	0,025	0,038
12	Zn	0,0043	0,013	0,14	0,052	0,014	0,016	0,023	0,041
13	Mo	0,00047	0,00045	0,00185	0,0005	0,00075	0,00155	0,00125	0,00065

The dry and ashless organic part of the liquid and solid phase is nothing but nitrocarbon. The technique for its determination is described in [12]. The yield of nitrocarbon was calculated from the organic matter of the initial coal.

Alkali-soluble organic substances were extracted from oxidized coal with a 1% aqueous solution of sodium hydroxide in a tenfold amount relative to the weight of the coal, the extraction time was 2 hours at the boiling temperature [1]. Triple extraction was used. The completeness of the extraction was controlled by the color of the extractant - the latter became colorless with the complete extraction of humic acids. The solid phase was separated from the liquid by centrifugation. The total volume of the solution was measured. An aliquot was taken from it, dried to constant weight, weighed,

and then calcined. The difference between the dried sediment and the ash part gave us the amount of alkali-soluble organic substances [1,13].

The solid phase of oxidized coal after separation of alkali-soluble organic substances from it is residual coal. It was thoroughly washed with distilled water, then dried to constant weight, and the yield was determined in terms of organic mass. The difference between the amount of alkali-soluble organic substances and humic acids gives the content of fulvic acids in the oxidized coal.

Table 3. Influence of technological parameters on the process of oxidation of the Fan-Yagnob deposit

№ samples corresponds to the numbers in table 1	Nitric acid concentration, %	Duration of oxidation, min	Ratio coal: acid	The degree of release of HNO ₃ into the gas phase, % relative initial mass	HNO ₃ content in the filtrate and wash water after oxidation, %		Humidity, %	Ash content, %	Organic mass of coals (OMC), %	Yield of humic acid on OMC, %
					Filtrate	Flushing water				
5.2	30	30	1:0,5	90,14	-	4,09	3,0	25,03	72,24	1,36
5.3			1:1	50,49	23,81	6,49	3,12	24,57	73,08	1,78
5.4			1:2	24,19	28,04	7,31	3,45	23,01	74,12	2,74
5.6	40	30	1:0,5	70,58	-	3,46	3,14	24,0	72,03	2,58
5.7			1:1	37,06	30,87	8,57	3,76	23,14	73,18	5,37
5.8			1:2	20,36	35,91	12,63	3,90	21,18	74,23	7,013
5.10	50	30	1:0,5	58,92	-	3,78	3,22	23,07	73,32	3,68
5.11			1:1	31,14	26,65	9,32	3,88	22,41	74,55	6,16
5.12			1:2	16,63	46,62	16,38	4,01	21,04	76,01	12,03
5.13	30	5	1:1	45,38	20,79	7,56	3,01	23,89	74,13	2,42
5.14		10	1:1	48,38	24,57	6,61	3,10	23,36	74,78	3,013
5.15		20	1:1	47,75	25,33	7,12	3,18	22,54	75,09	4,61
5.16		40	1:1	47,12	22,68	6,93	3,34	22,01	75,54	5,96
5.17	40	5	1:1	35,57	33,58	10,08	3,01	22,65	75,01	3,04
5.18		10	1:1	36,47	32,32	9,072	3,18	22,34	75,31	3,39
5.19		20	1:1	36,73	22,81	9,26	3,61	22,09	75,82	4,013
5.20		40	1:1	38,81	-	7,18	3,93	21,52	76,03	6,16

5.21	50	5	1:1	29,03	35,6	14,87	3,04	22,87	76,35	3,89
5.22		10	1:1	29,21	41,58	14,49	3,38	22,56	77,0	4,51
5.23		20	1:1	30,92	34,65	10,58	3,76	22,38	77,34	6,03
5.24		40	1:1	31,8	-	9,64	3,96	22,12	77,80	6,84

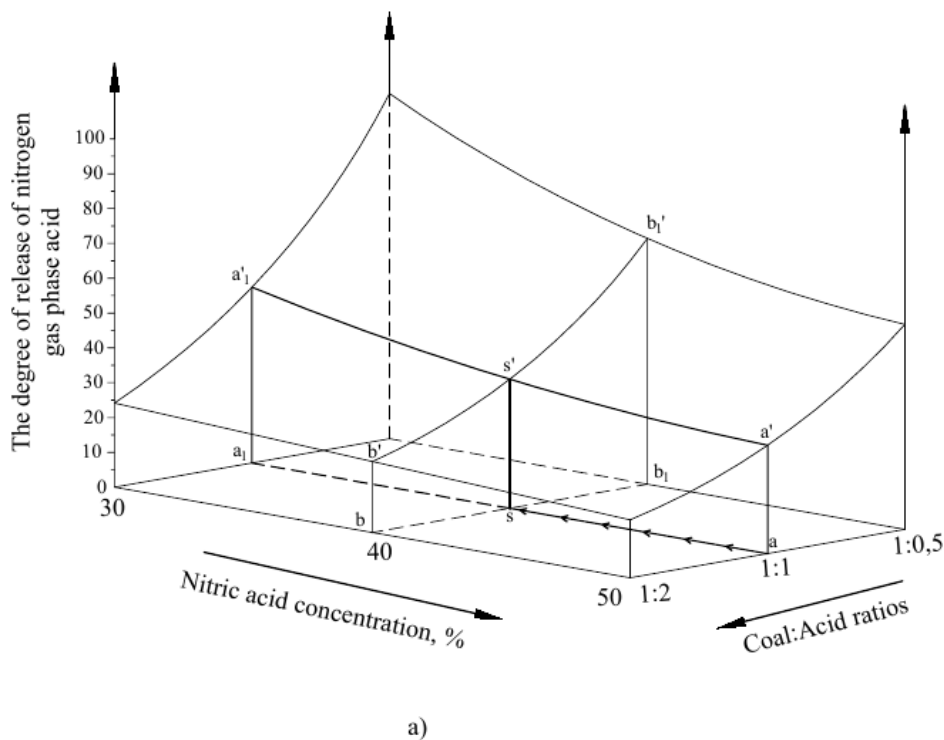
Nitrogen oxides released during the oxidation of brown coal with a mixture of nitric and sulfuric acids were determined [1]. Using a water jet pump, they were passed through absorbers with 0,5n NaOH solution. All solutions were collected together, brought to the mark of 500 ml, from which an aliquot was taken to determine nitrogen according to Kjeldahl [14].

The results of the experiments are given in table 3.

Common to all results is the following: with an increase in the concentration of nitric acid, the ratio of coal: HNO_3 and the duration of oxidation in the products, the content of water-soluble and alkali-soluble substances, nitrocarbon, humic and fulvic acids increases, the loss of nitrogen oxides increases, the ash content decreases. The dependence of the content of nitrocarbon and humic acids on the concentration of nitric acid is not linear. With an increase in the concentration of nitric acid from 30 to 50%, the effect of the coal: HNO_3 ratio on the content of nitrocarbon and humic acids increases [1].

The table shows that, depending on changes in technological parameters, the content of nitric acid in the filtrate and wash water ranges from 20,79 – 46,62 and 3,465 – 16,38%, respectively. That is, the concentration of nitric acid is reduced by 3,38 – 9,21%. The content of OMC increases by more than 77%, and the initial content of HA increases by more than 10 times. The dominant indicator of this stage is the degree of release of nitric acid into the gas phase and the content of humic acids in the products after oxidation. For a visual representation of the influence of technological parameters on the indicators of the obtained data, they are shown in the form of a nomogram in figs. 1 and 2. From fig.1a shows that with a decrease in the concentration of nitric acid, the degree of release of nitric oxide into the gas phase increases, and with an increase in the ratio of coal: HNO_3 from 1:2 to 1:0,5, its effects are enhanced and its rate reaches more than 90%. This indicates that the reaction of formation of nitrohumates is

practically absent. This opinion is confirmed by fig.2 a. Figure 2a shows that indeed, at low concentrations of nitric acid with a decrease in the ratio of coal: HNO_3 from 1:0,5 to 1:2, the content of HA increases monotonously, with an increase in the concentration of nitric acid, its action increases. When coal is oxidized with 50% concentration of nitric acid and the ratio of coal: HNO_3 - 1:2, the yield of humic substances reaches a maximum.



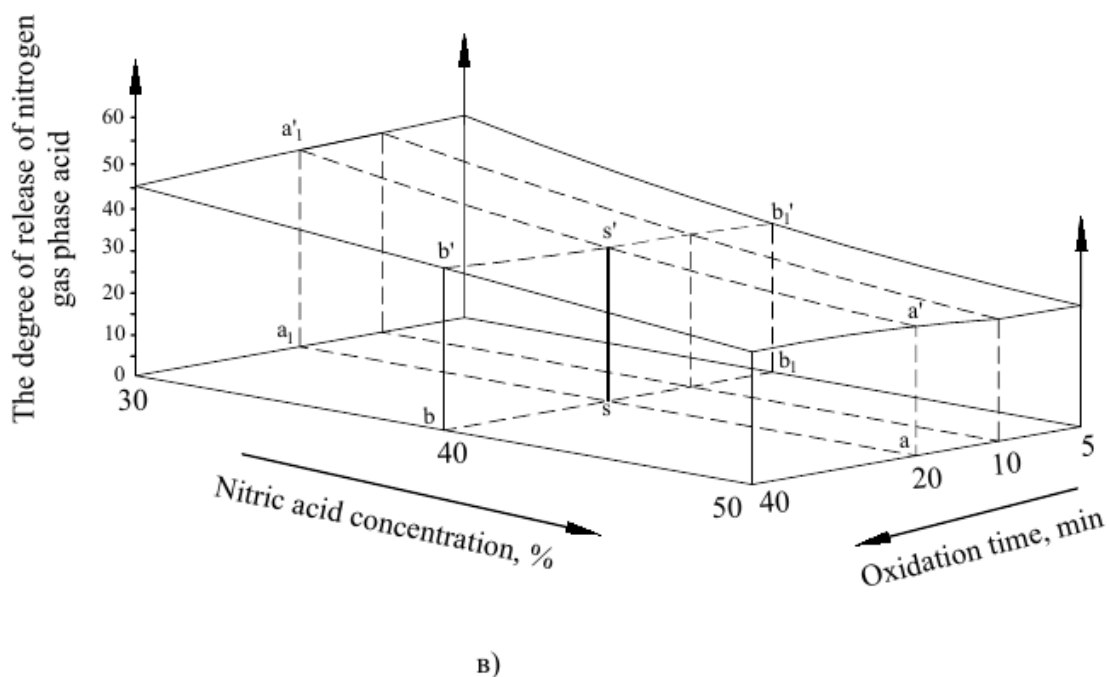
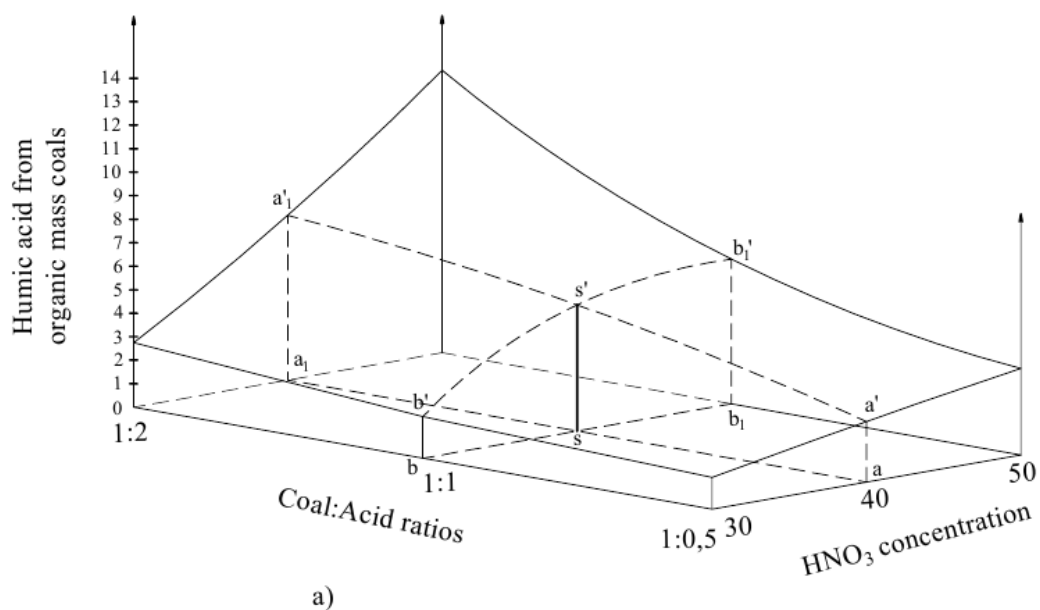


Fig. 1. Change in the degree of release of nitric acid into the gas phase depending on the concentration of nitric acid and the ratio of C:A (a), the duration of oxidation (b) (sample No. 5 "Fan-Yagnob Mine" eastern flank)



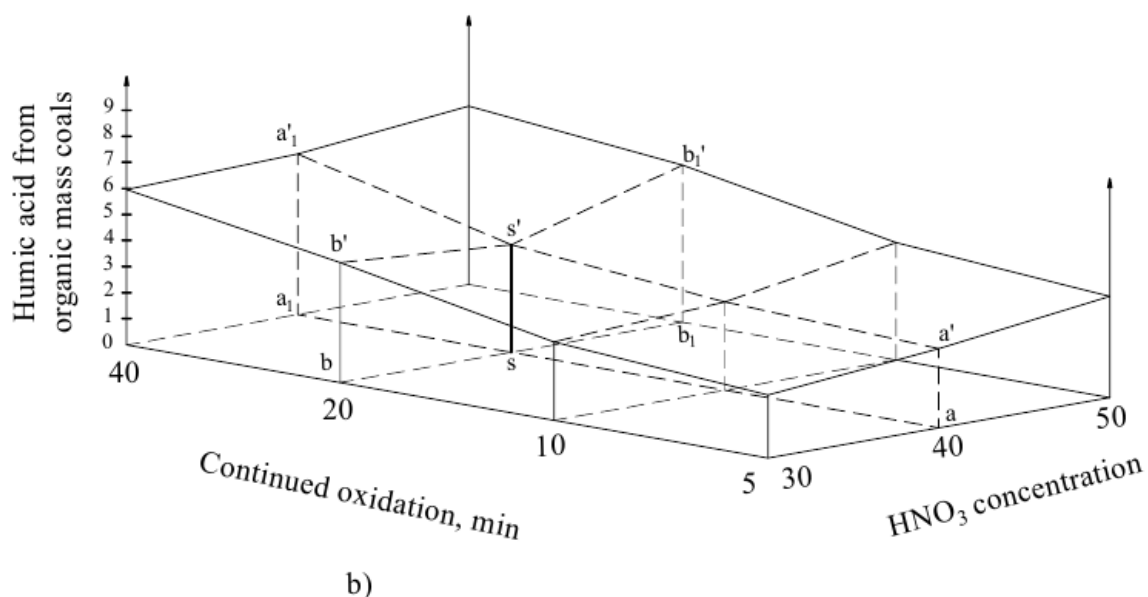


Fig. 2. Nomogram for determining the degree of coal oxidation depending on the concentration of nitric acid, the ratio of nitric acid: coal (a) and the duration of oxidation (b) in sample No. 5 "Fan-yagnob Mine" (eastern flank).

Therefore, the oxidation of other samples was carried out under these conditions. We studied the kinetics of their oxidation. The result of experimental studies is given in table 4 and figure 3.

Table 4. Kinetics of the process of oxidation of coal samples from the Shurab and Fan-Yagnob deposits under optimal conditions (C:A ratio - 1:2, oxidation temperature - 45 °C, nitric acid concentration - 50%)

№ experience	№ samples corresponds to the numbers in table 1	Duration of oxidation, min	The degree of evaporation, %	HNO ₃ content in filtrate and wash water		Humidity, %	Ash content, %	Organic mass of coals (OMC), %	Yield of humic acid on OMC, %
				Filtrate	Flushing water				
1	1	30	7,84	-	26,74	7,01	2,03	91,01	62,44
2		60	11,02	24,76	26,46	7,14	1,97	91,89	66,63
3		90	14,47	23,94	27,09	7,36	1,95	91,92	69,75
4		120	16,15	22,37	25,52	7,57	1,89	92,03	74,12
5	2	30	2,98	-	26,77	4,45	9,01	86,04	56,53

6		60	3,13	33,39	31,5	5,02	9,0	86,87	62,69
7		90	7,48	27,09	23,94	5,27	8,92	87,02	67,62
8		120	11,56	23,93	24,57	5,33	7,86	87,53	72,22
9	3	30	0,86	-	21,7	6,09	3,0	90,06	64,08
10		60	1,43	28,48	41,58	6,34	2,93	90,80	72,12
11		90	1,74	24,57	24,57	6,87	2,18	91,08	75,58
12		120	10,46	22,93	22,37	7,05	2,0	91,27	79,27
13	4	30	3,06	-	22,01	6,03	13,12	80,04	55,54
14		60	3,75	33,39	30,56	6,48	12,95	80,85	57,04
15		90	4,72	28,35	25,83	6,92	12,31	81,07	59,23
16		120	14,92	27,55	22,37	7,09	12,11	81,36	61,01
17	5	30	2,13	46,62	16,38	4,01	21,04	76,01	12,03
18		60	2,39	34,02	22,68	3,56	21,00	76,74	13,47
19		90	2,55	32,13	15,44	3,84	20,91	77,81	14,04
20		120	3,78	30,24	17,01	4,0	20,05	77,93	16,07
21	6	30	2,12	-	23,98	3,0	20,03	76,02	12,12
22		60	2,45	34,65	27,91	3,27	19,08	76,91	13,79
23		90	2,67	31,87	13,36	3,78	18,92	78,04	14,89
24		120	11,28	30,19	12,35	3,98	18,06	78,86	17,28
25	7	30	1,42	-	24,67	4,06	15,01	81,03	16,42
26		60	1,54	37,81	21,42	4,32	14,87	81,95	17,71
27		90	2,48	32,76	11,66	4,51	14,62	82,07	18,86
28		120	7,02	31,25	15,75	4,69	14,07	82,38	20,65
29	8	30	3,53	-	22,94	3,84	37,05	59,04	49,41
30		60	3,84	39,69	30,24	4,07	36,04	60,96	50,79
31		90	8,53	37,49	16,07	4,28	35,32	61,43	53,69
32		120	12,97	36,64	20,79	4,67	35,02	61,89	55,31

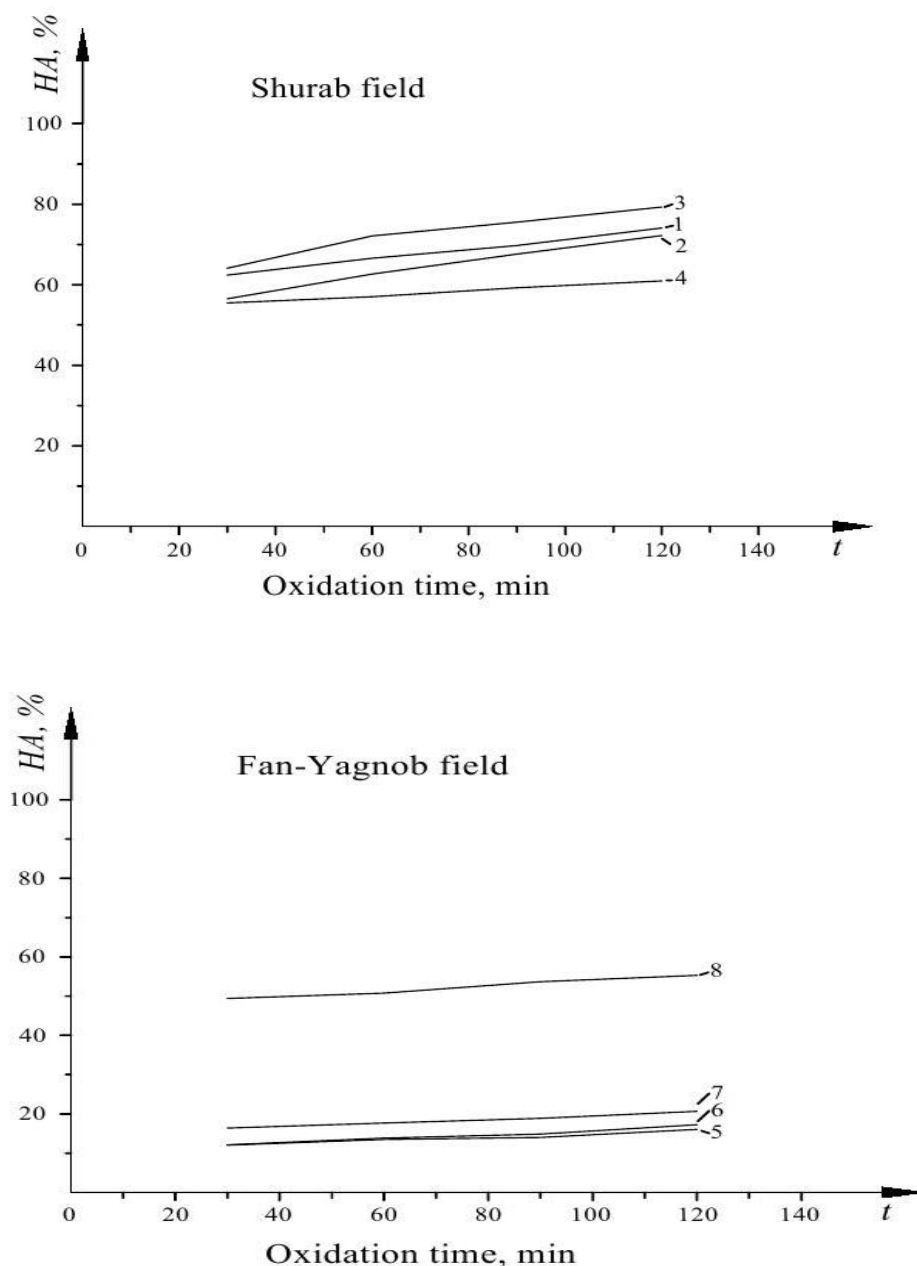


Fig. 3. Kinetics of oxidation of coal samples under optimal conditions. The sample numbers correspond to those in table 1.

From table 4 and fig 3. It can be seen from Table 3 that the duration of the oxidation process has practically no effect on the OMC content. Its content increases by only 0.5 - 1.5%, and the degree of oxidation increases by 10 - 15%. The main increase is observed within 90 minutes, with an increase in the duration of the oxidation process, the yield of humic acids increases slightly, however, the degree of release of nitrogen

oxide into the gas phase increases by 3-4 times. Therefore, the optimal oxidation time is considered to be no more than 90 minutes.

Table 5. Elemental composition of the liquid phase after nitric acid oxidation

№ samples corresponds to the numbers in table 4	Content of elements, g/l								
	B	Na	Mg	Al	P	K	Ca	Mn	Fe
2	0,004	0,0019	0,0067	0,11	0,00078	0,21	43	0,1	0,031
30	0,0015	0,082	0,42	0,98	0,0018	0,45	0,0057	0,16	0,34

Continued table 5

№ samples corresponds to the numbers in table 4	Content of elements, g/l								
	Co	Ni	Cu	Zn	Rb	Mo	Pb	Th	U
2	0,00078	0,0065	0,017	0,01	0,0001	0,000066	0,00071	0,00018	0,000055
30	0,039	0,07	0,066	0,44	0,0079	0,00081	0,018	0,0013	0,00067

Tables 5 and 6 give the elemental composition of the liquid phase and ash of oxidized coal obtained by mass spectrometric analysis (ICP-MS).

Table 5 shows that when coal is oxidized, metals pass into the liquid phase: Ca, Mg, Al, K and Na and their content is: 0.0057 - 43; 0.0067 - 0.42; 0.11 - 0.98; 0.21 - 0.45 and 0.0019 - 0.082 g/l, respectively. It should be noted that a sufficient amount of microelements such as Mn, Fe and Zn passes into the solution.

Table 6 gives a comparative analysis of the solubility of cations during the oxidation of various samples of coals. Table 6 shows that depending on the type of initial coal samples, the degree of dissolution of Ca, Mg, Mn and Fe varies in the intervals: 23,07 – 87,2; 21,87 – 89,23; 36,9 – 88,50 and 31,06 – 81,61%, respectively. It should be noted that the content of some elements in oxidized coals increases. For example, B and Na in the sample of the Shurob deposit decreases, and K and P in the Fan-Yagnobskoy deposit increase in almost all samples. The data show that these elements are in the form of acid-insoluble minerals.

Table 6. Elemental Composition of Ash from Initial and Oxidized Coal Samples

№ samples corresponds to the numbers in table 1	Content of elements, mass, %											
	B *			Na *			Mg *			P		
	original	oxidized	Δ	original	oxidized	Δ	original	oxidized	Δ	original	oxidized	Δ
1	0,0027	0,002	-83,54	1,6	1,4	-80,56	5,4	3,3	-86,42	0,078	0,085	+75,79
2	0,0024	0,0013	-69,53	1,2	0,6	-71,88	2,2	0,76	-80,57	0,1	0,082	-53,88
3	0,0025	0,0014	-83,2	1,8	1,1	-81,67	3,9	1,4	-89,23	0,076	0,084	+66,84
4	0,0016	0,0013	-51,99	5,9	2	-79,97	4,5	1,2	-84,24	0,09	0,082	-46,16
5	0,0032	0,015	+218,1	0,27	0,67	+68,39	0,53	0,51	-34,7	0,13	0,24	+25,28
6	0,002	0,0066	+144,4	0,41	0,55	+0,638	0,81	0,65	-40,56	0,14	0,17	+10,06
7	0,0018	0,0078	+195,4	0,26	0,47	+23,25	0,4	0,4	-31,82	0,1	0,13	+11,37
8	0,0016	0,0099	+397,7	0,25	0,53	+70,51	0,35	0,34	-21,87	0,097	0,12	+0,499

Continued table 6

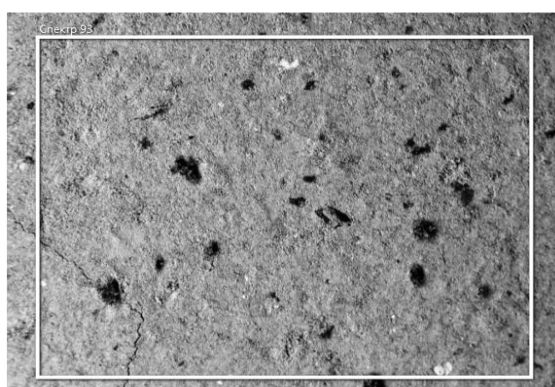
№ samples corresponds to the numbers in table 1	Content of elements, mass, %											
	K			Ca			Mn			Fe		
	original	oxidized	Δ	original	oxidized	Δ	original	oxidized	Δ	original	oxidized	Δ
1	0,4	0,55	+69,45	20	14	-84,45	0,088	0,058	-85,36	2,9	2,4	-81,61
2	0,36	0,37	+42,19	10	3,1	-82,56	0,035	0,012	-80,71	6,4	2,6	-77,15
3	0,4	0,46	+65,5	15	6,4	-87,2	0,06	0,023	-88,5	5,3	4,6	-73,96
4	1,6	1,4	-48,3	11	11	-40,91	0,068	0,024	-79,14	6,4	4,5	-58,45
5	2,9	4,2	+1,72	0,36	0,28	-47,22	0,0057	0,0053	-36,9	1,2	1	-43,45
6	3	4,6	+13,57	1	0,43	-68,15	0,026	0,0058	-83,48	4,2	0,96	-83,07

7	2,7	3,4	+14,14	0,31	0,29	-36,22	0,011	0,0036	-77,69	2	0,77	-73,75
8	3,3	3,7	+9,821	0,23	0,22	-23,07	0,01	0,0054	-56,57	1,4	1,2	-31,06

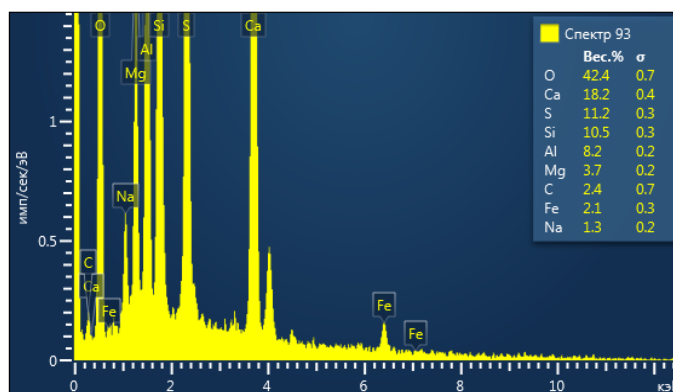
Continued table 6

№ samples corresponds to the numbers in table 1	Content of elements, mass, %											
	Co			Cu			Zn			Mo		
	original	oxidized	Δ	original	oxidized	Δ	original	oxidized	Δ	original	oxidized	Δ
1	0,0013	0,0018	+69,23	0,012	0,028	+48,15	0,0043	0,0088	+54,53	0,00047	0,00063	+70,22
2	0,00078	0,00052	-62,5	0,045	0,023	-71,25	0,013	0,0054	-76,63	0,00045	0,00065	+18,75
3	0,0033	0,0036	+67,27	0,01	0,028	+16	0,14	0,029	-93,79	0,00185	0,00365	+40,81
4	0,0014	0,0012	-49,35	0,014	0,016	+32,47	0,052	0,018	-79,55	0,0005	0,0006	+29,09
5	0,0017	0,0021	+16,17	0,02	0,033	+11,97	0,014	0,014	-32,14	0,00075	0,00115	+4,052
6	0,0019	0,002	+22,03	0,025	0,024	-28,89	0,016	0,013	-39,82	0,00155	0,00115	-45,04
7	0,0032	0,0024	-48,87	0,025	0,022	-40	0,023	0,012	-64,43	0,00125	0,00115	-37,27
8	0,0042	0,0011	-78,94	0,038	0,016	-66,13	0,041	0,012	-76,46	0,00065	0,00065	-19,57

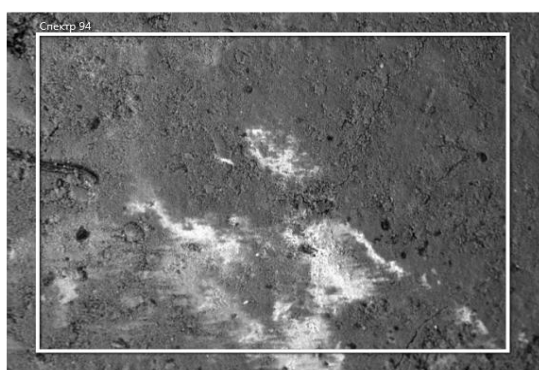
Электронное изображение 84



250µm



Электронное изображение 85



250µm

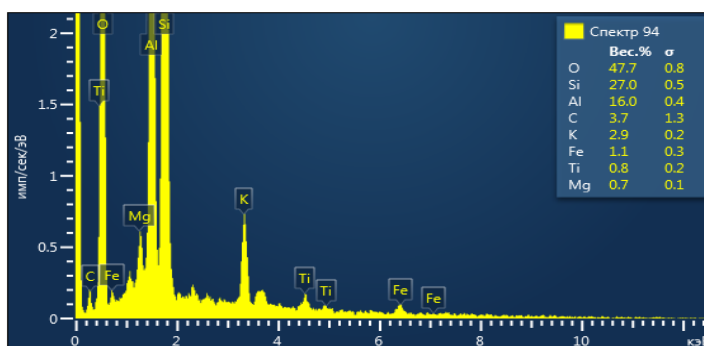


Fig. 4. Energy dispersive spectra of ash. The sample numbers correspond to the numbers of samples No. 1 and samples No. 8 (table 4)

Elemental composition of samples

Elements	Content, %		Elements	Content, %	
	Sample number			Sample number	
	1	8		1	8
C	2,35	3,73	S	11,2	-
O	42,44	47,71	Ca	18,19	-
Na	1,29	-	Fe	2,11	1,13
Mg	3,74	0,7	K	-	2,94
Al	8,15	16,0	Ti	-	0,77
Si	10,53	27,02			

Figure 4 shows the energy dispersive spectrum of ash after oxidation.

Table 4 shows that all Shurab samples contain: C, O, Mg, Al, Si and Fe. Coals from the Shurob deposit also contain Na, S, and Ca. It should be emphasized that the ash of Fan-Yagnob coal contains a significant amount of potassium – 2,94%.

Conclusion

Thus, the above data show that coal from the Shurab deposit and even its waste materials are suitable raw materials for the production of plant growth stimulants. It has been established that during the oxidation of coal from the Shurab deposit a ratio of coal: HNO₃ is to 1:2 and a temperature of 45 ° C for 90 minutes, it is possible to obtain oxidized coal with a content of 59,24 – 75,58% HA on OMC, suitable for obtaining plant growth stimulants and organomineral fertilizers.

List of used literature:

1. M.O.Zhumanova, N.Usanboyev, S. S.Namazov, B. M. Beglov."Oxidation of brown coal of Angren deposit with a mixture of nitric and sulfuric acids", Russian Journal of Applied Chemistry, 2010
- 2.Perminova I.V., Zhilin D.M. Humic substances in the context of green chemistry // Green chemistry in Russia. - M: Publishing House of Moscow State University, 2004, - S. 146-162.
2. Zabramny D.T., Pobedonostseva O.I., Pobedonostseva N.I., Umarov T.Zh. Carbohumic acids and their use. - Tashkent: Fan, 1980 - 153 p.
3. Kukharenko T.A. On the methods of extracting humic acids from peat and coal // Chemistry of Solid Fuel -1980, No. 5, - P. 87-94.
4. Lida Bondareva, Nadejda Kudrasheva. "Direct and Indirect Detoxification Effects of Humic Substances", Agronomy, 2021
5. Glebko A.I., Ulkina Zh.I., Kosheleva L.P., Vasilevskaya N.A., Maksimov O.B. New methods for determining functional groups in humic acids // New methods for studying humic acids. - Vladivostok, 1972, - S. 33-49.
6. Golovin G.S., Lesnikova E.B., Artemova N.I., Lukicheva V.P. Use of humic acids in solid fossil fuels. - 2004, No. 6, - S. 43-49.

7. Semenova S.A., Fedyaeva O.N., Patrakov Yu.F. Liquid-phase ozonation of highly metamorphosed coal // Chemistry for sustainable development. - 2006, v.14, No. 1, - S. 47-52.
8. Tajiev A.T. The method of oxidative-hydrolytic splitting of brown and low-metamorphosed coals // Reports of the Academy of Sciences of the UzSSR. - 1961, No. 2, - S. 37-41.
9. Moldybaev A.B., Krichevsky L.A. Application of the method of rational planning of the experiment in the process of oxidation of brown coal of the Maykubenskoye deposit // Chemistry of Solid Fuel. - 1981, No. 6, - S. 20-22.
10. Usanbaev N., Namazov Sh.S., Beglov B.M. Oxidation of brown coal of the Angren deposit with nitric acid // Chemical industry. - 2006, v. 83, No. 2, - S. 55-61.
11. Ilyushenko R.G., Spitsyn A.K. Obtaining cyclic oxidation products from Donetsk coals of different grades // Research, use and standardization of coals. - M.: Nedra, 1965, - S. 71-77.
12. Kukharenko T.A., Shapiro S.A. Fundamentals of technology for the production of humic acids // Humic fertilizers. Theory and practice of their application. - Kharkov: Publishing House of Kharkov State University, 1957, - S. 39-45.
13. Pozin M.E. Guide to practical exercises on the technology of inorganic substances. - L.: Chemistry, 1980, - 368 p

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["Direct and Indirect Detoxification Effects of
Humic Substances", Agronomy, 2021](#)

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