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Studying The Processes of Oxidation of Plant Residues to Increase the Yield of Extractive Substances

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ABSTRACT: The article presents the results of studying the processes of oxidation of plant residues (RO) with nitric acid depending on the acid concentration, temperature, duration and weight ratio. As a result of the research, it was revealed that it is possible to increase the extractive substances extracted with 1% sodium hydroxide solution from 4.37% to 48.37% if 30% HNO3 is oxidized at 400 C for 2 hours. The losses of nitrogen oxides into the gas phase during the oxidation process were determined. The elemental composition of the ash of the original RO was determined, as well as the chemical composition of the original and oxidized RO, extractive substances and insoluble organic substances of RO.

I.INTRODUCTION

In the world, agriculture is an important sector of the economy, the main source of food. Providing the agro-industrial complex with various fertilizers necessary for maintaining soil fertility and for the efficient use of water and land resources is the main factor in obtaining a high and high-quality crop from agricultural crops.

In recent years, all over the world, special attention has been paid to the production of fertilizers containing humic substances, plant growth and development stimulants, humic ameliorants using organic resources, as well as their use in agriculture due to the decrease in the content of humic substances in the soil.

Humic substances are high-molecular organic compounds of a complex physico-chemical structure, formed in soils, peat, coals, and other natural bodies, widely distributed in nature. They accumulate nutrients, participate in the migration of cations, reduce the negative effect of toxic substances, affect the development of organisms and the heat balance of the planet. They are stable, high molecular weight, polydisperse, contain various functional groups, amino acids, polysaccharides, and benzoic fragments [1, 2].

There are several groups of humic substances: humic acids, soluble only in alkaline solutions; hymatomelanic acids extracted from the crude residue of humic acids with ethyl alcohol; fulvic acids, soluble in water, alkaline and acidic solutions; humin, a practically insoluble organic substance that cannot be extracted from natural bodies. The composition and properties of these substances vary depending on the source, but even in preparations obtained from the same source (the same type of soil, peat, coal), they are heterogeneous, polydisperse and are represented by a large set of molecules similar in structure, but not identical. All these substances, except for humin, are the most mobile and reactive components of humic substances actively involved in chemical processes in ecosystems [3–5].

The basis of the molecular skeleton of humic acids is an aromatic system containing carboxyl (-COOH), hydroxyl (-OH), carbonyl (-C=O), methoxyl (-OCH3), phenolic and quinoid groups as substituents; ether, ester, aldehyde groups. Among the oxygen-containing functional groups, hydroxyls predominate, followed by carboxyl groups. Humic acids depending on pH can be divided into a number of fractions with different molecular weights. However, all fractions contain practically the same functional groups, which indicates the commonality of their structure. Therefore, humic acids are not a clearly defined class of compounds, but are a group of macromolecular compounds with slightly different composition, but with a common type of structure and common properties. According to the chemical composition, these are high molecular weight aromatic and aliphatic hydroxycarboxylic acids, the fragments of which are interconnected by oxygen and methylene bridges [6, 7].

The elemental composition of humic acids is not the same: 57.5-64.2% - C; 4.3-5.4% - H; 29-34% - O; up to 4% - N. Nitrogen is part of melanoids - products of condensation of carbohydrate fragments with amino acids formed during the breakdown of proteins and carbohydrates. Variations in the elemental composition depend on the nature of the initial biomass, in particular, lignins. A genetic relationship between humic acids and lignin has been established. With the gradual destruction of lignin by fungi (white and brown rot), some of the simplest compounds (molecule fragments) are included in the metabolism of microorganisms, and high-molecular humic substances are formed from the rest. In the case of a destructive process (boron rot), humic and hymatomelanic acids are formed; in the case of corrosion destruction (white rot), fulvic acids are formed [8].

Fulvic acids are light-colored specific amorphous acids that give solutions of a golden yellow color in water and aqueous solutions of acids. Soluble in water and solutions of mineral acids, as well as light-colored amorphous fulvic acids remaining during precipitation from alkaline solutions of humic acids, have higher H : C atomic ratios than the corresponding humic acids. Their optical density is lower in comparison with humic acids of the same sources, and differs somewhat in accordance with the H : C ratio; lower for a sample from peat than for oxidized coal. Fulvic acids can be separated into two fractions with the help of ethyl ether [9,10].

The work [11] presents data on the separation of acids into alcohol-soluble (hymatomelanic) and insoluble (humic). The separation was carried out by extraction in a Soxhlet apparatus. The mechanism of release of humic and hymatomelanic acids is not yet completely clear. There is reason to believe that these processes are somewhat more complicated than the separation of a mechanical mixture of acids. Hymatomelanic acids are found mainly in the fraction of humic acids that is separated from oxidized coals with aqueous alkali without preliminary treatment with hydrochloric acid. On the example of the formation of hymatomelanic acids, the idea of a series-parallel course of the reaction of coal oxidation in the course of weathering is confirmed. Hymatomelanic acids contain methoxy, carboxyl and hydroxyl groups; they are characterized by a high carbon content (more than 60%). Hymatomelanic acids can be formed both from the decomposition products of organic residues and from derivatives of the oxidative-hydrolytic degradation of humic substances under the action of oxygen and moisture. Distinctive features of hymatomelanic acids are: high values of the atomic ratio of hydrogen to carbon (H/C) - more than one, high negative degree of oxidation, low extinction coefficients, high absorption intensity in the range of 1700-1720 cm-1 [12, 13].

Humic acids are prone to oxidation-hydrolytic and tautomeric transformations, have a high redox potential and form complexes with metals of variable valence. They are thermodynamic open systems, since their properties depend significantly on external conditions. The reactivity is mainly determined by their radical nature and the character of aromatic hydroxyoxocarboxylic acids [14-17].

Humic acids, depending on the pH of the medium, exhibit either acidic or alkaline properties due to the release or acceptance of hydrogen ions, which determines the acid-base buffer properties of these natural compounds. Able to enter into ion-exchange reactions with cations and anions. The magnitude of the degree of electrolytic dissociation of humic substances, like any electrolytes, increases with a decrease in the concentration of the solution. Therefore, when the solution is diluted, humic acids will dissociate into ions, and associate when concentrated. When diluted, the osmotic pressure of a solution of humic acids, although it will decrease, will be partially compensated due to dissociation; when concentrating due to association, the opposite picture will be observed. In other words, aqueous solutions of humic substances are capable of exhibiting isotonic buffering. [18].

Humic acids form complexes with metal ions - this is an obligatory link in soil formation. Studies have established that the cause of the accumulation of rare elements in organic matter is the processes of sorption, complex formation, and ion exchange. Under certain conditions, they form insoluble salts with uranium, copper, germanium, etc. [19, 20].

Humic substances in soils perform various functions, giving soils stable characteristics, determining their many important properties and functions, the main of which are: accumulative, transport, regulatory, protective and physiological.

The accumulative function is characteristic especially for humic acids. The essence of this function lies in the accumulation in the form of humic substances of the most important nutrients of living organisms, organic compounds that carry energy reserves or are directly necessary and assimilated by microorganisms or plants. It is well known that it is in the form of humic substances that up to 90-99% of all nitrogen, half or more of phosphorus and sulfur accumulate in soils. In the same form, potassium, calcium, magnesium, iron and almost all trace elements necessary for microorganisms are accumulated and stored for a long time.

The transport function of humic acids lies in the fact that humic acids, along with poorly soluble, stable compounds with metal cations, can also form stable, but soluble and capable of geochemical migration compounds. It is well known that, at pH values common to most soils, iron is practically immobile. The dominant form of iron hydroxide with a solubility product cannot cause a noticeable movement of ionic iron in the soil profile. However, iron migration is a well-established fact. For iron, as well as for cations of many other metals, the dominant migration form is represented by complex organomineral compounds, in which fulvic acids play a predominant role. Most microelements, a significant part of phosphorus and sulfur compounds migrate actively in this form.

The regulatory function of humic substances is complex. It combines many phenomena and processes in soils. In the regulatory function of humic substances, several main components are distinguished: 1) the formation of soil structure and water-physical properties of soils; 2) regulation of the ion exchange reaction between solid and liquid phases; 3) influence on acid-base and redox regimes; 4) regulation of the nutritional conditions of living organisms; 5) regulation of the thermal regime of soils and atmosphere.

The protective function of humic substances is known, but insufficiently studied. In general, it can be argued that humic substances in the soil protect or preserve biota, pores in the event of various kinds of adverse extreme situations. It is known that humus soils are better resistant to drought or waterlogging, they are less susceptible to erosion. Humic substances quite strongly bind many radionuclides, detergents, pesticides, thereby preventing their entry into plants or other negative effects. The physiological function is associated with the role of humic substances as carriers of essential amino acids, some vitamins, and antibiotics. [21-23].

The influence of humic substances on the physiological activity of plants is diverse. In works [24-26], it was shown that humic substances are able to enter the plant organism when they are contained in the soil solution in thousandths and ten-thousandths of a percent. Under the action of humic substances, root formation is activated in plants, due to a change in the selectivity of cell membranes, the supply of water and nutrients is enhanced, so that humic compounds positively affect all phases of the mitotic cycle of cells and cause an increase in the value of the mitotic index by 1.5 times. They are able to participate in physiological and biochemical processes, activating the activity of enzymes of redox reactions, increasing the intensity of respiration, the productivity of photosynthesis, the absorption of mineral elements and the use of absorbed phosphorus for the synthesis of protein substances. The action of such compounds is most actively manifested when external conditions deviate from the norm, in particular, the conditions of mineral nutrition, fluctuations in air and soil temperature, moisture and oxygen content in the air and the root sphere. In extreme conditions, when the course of bioenergetic processes is disrupted and cannot be restored without additional energy expenditure, their adaptogenic ability manifests itself, regulating the synthesis of nucleic acids, enzyme proteins and constituent proteins, the processes of repair and regeneration.

The soils of Uzbekistan are classified as poor in terms of the content of this most important substance. The irrigated land fund of Uzbekistan consists mainly of sierozems, sierozem-meadow, takyr-meadow soils and, to a lesser extent, gray-brown and desert sandy soils. The humus content in them is relatively low; in the arable horizon, its amount ranges from 1.2-0.8 (in gray, takyr and meadow soils) to 0.8-0.55 (in gray-brown and desert sandy soils), while in the same horizon of chernozems of chestnut soils humus contains 4-2% [27]. The specific gravity of soils with a low content of humus (0.8-1% in gray soils) is almost 2/3 of the area, with an average (1-1.2%) - 1/3, and with a high (1.2-1. 5% of the soil weight) - only 7% of the sown area [28]. The reserves of humus in the meter layer of soils of Uzbekistan are as follows (t/ha): light gray soil 82.8; typical serozem 78-79; typical dry sierozem 59.5; dark serozem 150.5; brown soil 318.6; meadow-marsh soil 139.2 [29].

In the process of agricultural production using land, part of the humus in the soil is gradually mineralized with the release of nitrogen and other nutrients, which are converted into a form that is assimilable to plants. In this case, the loss of humus can be 0.6-0.7 t/ha per year. With high yields of grain crops, the soil annually loses 0.5-1.0 t/ha of humus, while cultivating tilled crops, humus losses increase to 1.5-3.0 t/ha. It has been established that a 1% decrease in the content of humus in the soil leads to a decrease in the yield of agricultural crops by about 5 centners of grain units per hectare [30, 31].

The work notes that [32] modern high-intensity farming systems significantly expand the possibilities of purposeful regulation of crop productivity, however, they also increase the intensity of the circulation of substances and energy in agroecosystems, lead to an increase in the removal of nutrients from the soil by crops, which, often, due to objective reasons, are not replenished by applying with organic and mineral fertilizers. This violates the immutable law of nature, the law of return of nutrients, formulated back in 1840 by Liebig.

The problem of creating a positive balance of humus in the soil is one of the most urgent tasks in agriculture. Only with the optimal amount of humus in the soil is it possible to obtain a high effect from growing crops. In the reproduction of humus, the role of organic and WMD is indispensable.

One of the non-traditional sources of replenishment of HS reserves in irrigated soils can be plant residues. The rational use of plant residues in agriculture is one of the factors for maintaining and increasing soil fertility. The use of plant residues of agricultural crops for fertilizer contributes to an increase in the content of humus and nutrients in soils.

The modern farming system provides for the active use of plant residues as an organic or organomineral fertilizer. In plant residues, in addition to organic matter, the nitrogen content varies from 0.5 to 0.7%, and in the plant residue of peas it reaches up to 1.6%. The maximum value of potassium content was noted in oat straw 1.6%, in other crops it varies within 0.8-1.0%. The content of phosphorus in plant residues of agricultural crops is 0.2–0.3% [33].

The paper [34] presents the results of the effect of mineral fertilizers on the mineralization of humus in the plow layer of leached chernozem. The mineralization of humus was determined on a natural agricultural background and when various doses of mineral fertilizers were applied. For five years, the humus content in the variant without fertilizers in a layer of 0 ... 40 cm decreased from 6.27 to 6.01%, its mineralization coefficient was 0.8% of the humus content. The application of fertilizers for the planned yield of 3.0 and 4.0 t/ha slightly stimulated the soil microflora, the vital activity of which, in the absence of plant residues, reduced the humus content from 6.85 to 6.46%; the mineralization coefficient corresponded to the generally accepted values of 1.0% of the humus content. In the fields with a high agricultural background, which ensures the formation of grain crops from 5.0 to 6.0 t/ha, the soil microflora has become more active throughout the arable layer. Its activities led to a decrease in the humus content from 6.06 to 5.61%. The mineralization coefficient increased to 1.5% of the humus content.

In [35], a comparative assessment of organic fertilizers from manure and from plant residues is given, their equivalence in terms of agronomic efficiency and the advantage of plant residues are shown. Thus, in the link of crop rotation with row crops, the level of profitability of production against the background of the use of plant residues increased by 41%, and in the link of crop rotation without row crops - by 47% compared with manure. Straw and other plant residues should be used as organic fertilizers along with manure. This provides an increase in soil fertility and crop yields while reducing energy, material and labor costs for production, which at this stage is an important factor in agricultural production.

According to [36], on average, after harvesting crops, 4.42 t/ha of plant residues enter the soil, while the compensation for the removal of crops by crops due to the introduction of plant residues into the soil as organic fertilizers for nitrogen is 32.6%, phosphorus - 14.0 and potassium 37.8%.

However, plant residues do not always enter the soil, besides, plant residues entering the soil after harvesting are not completely converted into humic substances, as conditions are not always created in the soil for the transformation of plant residues into humic substances, especially in serezems. Therefore, the development of technologies for processing organic resources of humic nature, including plant residues into organic and organ mineral fertilizers and their application is relevant.

Plant residues are a complex set of chemicals. It has been established that the plant remains of various species contain basically the same substances, but in different proportions. The main ones are cellulose, hemicellulose and lignin, which form the cell wall and make up to 90-95% of the mass of absolutely dry wood. The remaining 5-10% are combined into a group of extractives, that is, extracted with various solvents without a noticeable change in composition. Under the conditions of a negative balance of humus in agriculture with its annual deficit and more, a real means of replenishing organic matter is the introduction of plant residues of agricultural crops after processing. The use of plant residues to obtain organic or organ mineral fertilizers is a promising direction [36].

It is known that the characteristic reactions for plant residues are interactions with electrophilic reagents, including nitric acid. In this paper, study the behavior of hydrolytic lignin when heated diluted with nitric acid. As a result of the nitrating action of nitrogen oxides, nitrolignins with a nitrogen content of no more than 3% were obtained. At the same time, the number of metaxyl groups decreased and carboxyl groups arose. Additionally, oxalic acid was isolated [37].

According to the method [38], lignin in three successively connected screw apparatuses is treated with nitrogen oxides with air, then with 53-58% nitric acid or diluted melange, which are fed in a dispersed state in an amount of 50-60% relative to dry lignin. The oxidized mass is continuously fed to the filter press, where excess acid is squeezed out, washed and neutralized. The resulting nitrated product dissolves in 1.5% ammonia solution by at least 70% and is used as a nitrogen-containing fertilizer that stimulates plant growth.

In [39], hydrolytic lignin was nitrated with a nitrating mixture containing nitric and phosphoric acids. They obtained a small yield of nitrolignin by using phosphoric acid and acetic anhydride. Nitrogen in nitrolignins contains 7.5-8%.

In the study of model compounds of lignin, she showed that during the nitration of 2 and 4 p. with an ether solution of nitric acid of 1-guaiacylpropinal -3, along with the nitration of the nucleus, demethoxylation is observed with the formation of orthoquinone. The author believes that demethoxylation of lignin during nitration occurs in this way [40].

In [41], the effect of dilute nitric acid on model compounds of lithine was studied. It was found that both in an aqueous medium and in the system of chloroforms of acetic acid, nitro derivatives of p-quinone are obtained as the final product. This is also confirmed by the data of Ley and Müller [42], who, upon nitration of model lignin compounds with nitric acid in absolute ether, obtained nitro derivatives of orthoquinones and considered this as evidence that lignin demethoxylation occurs with the formation of quinones.

The authors of [43] studied the behavior of monomeric and dimeric compounds simulating the structural units of lignin during fractional oxidation with dilute nitric acid and found that the stability of phenylpropane monomers depends on the nature of the side chain and oxygen-containing substituents present in the benzene ring. The authors believe that a large amount of oxalic acid is formed from lignin during the oxidation of structural elements with a dephenyl group. For polycarboxylic acids, the products of the oxidative-hydrolytic cleavage of lignin are characterized by physiologically active properties, which is associated with their quinone structure.

As a result of the oxidative-hydrolytic effect of nitric acid solutions on hydrolytic lignin, the subsequent neutralization of the pulp with ammonia water and mixing the resulting solution of ammonium salts of polycarboxylic acids with dry lignin, a nitrogen-containing fertilizer was obtained [44]. It was noted in [45] that the oxidation of an aqueous suspension of lignin with nitric acid is accompanied by the release of nitrous and carbon dioxide gases, which periodically foam and eject the reaction mass. To prevent emissions, an oxidation method has been developed, which consists in the fact that the initial suspension - lignin - water passes successively a number of columns, where it is gradually oxidized. Compressed air is fed into the column to keep the lignin in suspension. The mixture passes through 6 columns in 3 hours and receives all the calculated amount of nitric acid, however, the peak state is noted in the 2nd and 3rd columns. For additional oxidation and evaporation, the mixture is boiled for another 32 hours, then cooled and neutralized with ammonia to pH = 8-9. The neutralized solution is mixed with 9 parts of dried lignin for 3 hours. The composition of the lignin-stimulating fertilizer is, on average, the following, wt. %: lignin - 80-86, ammonium salts of polycarboxylic acids-10, $(NH_4)_2SO_4$ - up to 3, NH_4NO_3 up to I, ash - up to 6.

Based on the foregoing, the purpose of this work is to assess the possibilities of processing plant residues into valuable chemical products by oxidation.

The object of the study is coarsely ground plant residues (RO). RO was dried to an air dry state, then crushed to a particle size of 0.25 mm. After grinding, an average representative sample of RO was formed having the following composition (wt. %): moisture 6.86; ash 10.74; organic 82.4; the content of extractives extracted by 1% NaOH solution 4.37, the content of extractives extracted by water 1.22; Table 1 shows the results of mass spectrometric analysis (ICP-MS) of RO ash. It follows from the table that RO contains a number of trace elements necessary for the growth and development of plants.

Table 1
Results of mass spectrometric analysis of RO

Name and content of elements, in%							
Mg 2,77	Si 2.08	P 3,88	S 0.405	K 28,4	Ca 9,47	Mn 0,06	Fe 0,429
Zn 0,041	Br 0.0011	Rb 0.0243	Sr 0.0270	Ti 0,0411	Zr 0.145	Sn 0.0013	Re 0.0041

In order to increase the content of extractives i.e. For the conversion of PO into humic acids, fulvic acids, and other organic acids, the process of PO oxidation with nitric acid was studied.

The oxidation process was carried out at concentrations of nitric acid from 20, 30 and 40%, temperature from 30 to 60°C, duration from 30 to 120 min and weight ratio PO : HNO_3 from 1 : 1.0 to 1 : 2. Under the ratio PO : HNO_3 meant the ratio of the organic part of PO to nitric acid monohydrate. The experiments were carried out in a cylindrical reactor equipped with a thermostatic jacket and a stirrer. Acid was poured into the reactor, the set temperature was set, the stirrer was turned on, and a sample of crushed RO was loaded. At the end of the process, the reaction mass was divided into liquid and solid phases. The solid phase was washed with distilled water from nitric acid to a neutral reaction, dried to an air-dry state, and the ash content, moisture content, organic matter, and the yield of extractives were determined in it with a 1% sodium hydroxide solution. Ash content was determined according to GOST 11022-95, humidity - according to GOST 11014-91, organic matter - by the difference between 100 and the sum of the percentages of ash and moisture.

The contents of extractive substances of the initial RO and the solid phase of the oxidized RO with nitric acid were determined according to the procedure given in [3]. The results of the experiments are shown in tables 2-4. From Table. Figure 3 shows how the composition of oxidized PO changes depending on the concentration and norm of nitric acid. The amount of oxidized PO increases to 115.2% relative to the organic part of the original PO. At an HNO3 concentration of 30%, a ratio of PO : HNO3 = 1 : 1.6 at a temperature of 40°C and a duration of 2 hours, 42.42% of the original PO remains underoxidized. Main

Table 2.
Output of PO oxidation products (in % to the organic part of oxidized PO) depending on the rate and concentration of nitric acid (τ - 120 minutes, t - 40°C)

Oxidation products	Concentration HNO$_3$, %	Ratio PO : HNO$_3$					
		1 : 0,2	1 : 0,4	1 : 0,6	1 : 1	1 : 1,2	1 : 1,6
oxidized PO	20	98.3	101,5	102,3	104,2	104,2	105,1
	30	102,1	104,4	105,5	106,7	108,8	110,7
	40	103,6	105,3	107,7	109,7	112,7	115,2
Extractives 1% solution NaOH	20	43,34	43,93	45,08	45,68	45,81	45,94
	30	44,17	44,51	45,35	45,80	47,01	48,37
	40	45,59	44,79	46,04	46,37	47,55	48,87
Organic acids precipitated in an acidic environment	20	18,32	14,92	15,51	14,08	13,08	12,18
	30	16,97	14,36	14,40	13,59	12,43	11,26
	40	15,22	13,71	13,08	12,83	11,80	10,89
water soluble organic matter	20	1,22	2,53	3,09	3,95	4,31	5,07
	30	2,19	4,21	4,84	5,03	5,75	6,03
	40	4,91	5,77	6,64	7,45	6,79	8,93
Residual PO	20	55,44	53,53	51,83	50,37	49,88	48,99
	30	53,64	51,28	49,81	49,17	47,24	45,60
	40	49,50	49,44	47,32	46,18	45,66	42,42
Losses of nitrogen oxides (NO, NO2), in terms of nitrogen	20	5,01	4,79	3,54	3,12	2,57	2.12
	30	9,07	7,99	6,23	5,57	4,63	3,79
	40	14,94	12,22	11,13	11,07	9,45	8,28

Table 3
The yield of products of oxidation of plant residues depending on the temperature of the oxidation process

Process temperature	Determined components in % to the organic part					
	Oxidized PO	Extractives 1% solution NaOH	Organic acids precipitated in an acidic environment	water soluble organic matter	Residual PO	Losses of nitrogen oxides (NO, NO2), in terms of nitrogen
Concentration HNO_3 = 20%, ratio. PO : HNO_3 = 1 : 1,6, τ - 75 minutes						
30	103,3	44,19	7,93	1,76	54,05	3,12
40	106,2	45,86	9,84	3,59	50,45	4,21
50	101,4	42,28	8,82	9,56	48,16	8,84
60	96,5	40,74	6,28	11,65	47,61	14,54
Concentration HNO_3 = 30%, ratio. PO : HNO_3 = 1 : 1,2, τ – 75 minutes						
30	103,4	46,16	10,88	4,54	49,30	3,56
40	106,7	47,01	12,43	5,75	47,24	4,63
50	104,8	46,85	10,54	9,50	42,61	9,86
60	102,2	45,14	8,30	14,42	40,44	15,46

Table 4
Yield of PO oxidation products depending on the duration of the oxidation process

Oxidation time, Min	Detectable components in % to organic part					
	Oxidized PO	Extractives 1% NaOH solution	Organic acids precipitated in an acidic environment	water soluble organic matter	Residual PO	Losses of nitrogen oxides (NO, NO2), in terms of nitrogen
Concentration HNO_3 = 20%, ratio PO : HNO_3 = 1:1,6, temperature 40°C						
30	97,3	40,79	8,93	1,16	58,05	1,76
45	101,5	43,79	9,38	2,24	53,97	2,39
60	103,4	45,68	10,22	3,86	50,64	3,74
75	105,2	46,89	10,80	4,95	45,37	4,21
90	101,4	44,54	10,08	11,65	43,81	6,84
120	99,8	42,55	9,01	19,04	38,41	10,54
Concentration HNO_3 = 30%, ratio. PO : HNO_3 = 1:1,2, temperature 40°C						
30	98,3	41,52	11,06	3,04	55,44	1,88
45	101,4	43,25	11,34	4,23	52,52	2,81
60	103,8	46,52	11,67	5,36	48,12	3,21
75	106,7	47,01	12,43	5,75	47,24	4,63
90	104,8	45,91	10,44	11,95	42,14	9,84
120	97,4	44,48	9,96	19,14	36,38	14,45

The main goal of oxidation is to increase the content of alkali-soluble organic acids in RO, while it is successfully achieved from 4.37% in the original RO to 48.37% in the oxidized one. Relatively small (4.21%) with the above process parameters, the loss of nitrogen into the gas phase.

Table 3 shows the change in the composition of oxidized PO at HNO3 concentrations of 20 and 30%, ratio PO : HNO3 = 1 : 1.6 depending on temperature. Optimum oxidation parameters are observed at 40°C. At this temperature, we have the maximum amount of oxidized PO and the highest content of extractive substances in it (45.86 and 46.85%).

Table 4 shows the yield of PO oxidation products at a ratio of PO : HNO3 = 1 : 1.6, a temperature of 40°C, an HNO3 concentration of 30 and 40%, depending on the duration of the interaction of PO with nitric acid. From this table it can be seen that at a concentration of HNO3 = 30%, the maximum content of humic acids in oxidized coal can be achieved with a 75-minute interaction. Further increasing the duration of the oxidation process, we thereby increase only the loss of nitrogen oxides into the gas phase.

Thus, the study showed that the oxidation of licorice PO with nitric acid increases the content of extractive substances, which is the most valuable product for obtaining organic and organ mineral fertilizers, as well as plant growth stimulants.

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