

Oxidation Of Licorice Root Waste With Nitric Acid To Increase The Productivity Of Extractive Substances

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Abstract The results of studying the processes of oxidation of licorice root waste with nitric acid depending on the acid concentration, temperature, duration and weight ratio of waste: acid are presented in the article. It was shown that the amount of extracted substances in the waste in 1% sodium hydroxide solution can be increased from 5.87% to 49.68%, if the oxidation of 20% HNO₃ is carried out at 40°C for one hour with the weight ratio of the organic part of the waste to nitric acid monohydrate equal to 1: 1.6. Losses of nitrogen oxides into the gas phase during the oxidation process have been determined. The elemental composition of the ash of the original waste, the chemical composition of the original and oxidized waste, extractive substances and insoluble organic matter of the waste, the content of functional groups in them were determined.

Key words: oxidation, licorice root waste, nitric acid, extractives

Currently, more than thirty enterprises and companies of different forms of ownership in different regions of Uzbekistan are engaged in the cultivation and processing of licorice root. Licorice grows in the north-west of Uzbekistan in Khorezm, Bukhara regions, as well as in the Republic of Karakalpakstan. It grows in the valleys and deltas of the Amudarya and Syrdarya, in the mountains, along canals, in collectors, in saline swamps and marshy lands. [1].

Licorice is a herb of the legume family. Licorice leaves are used for medicinal infusions and decoctions, in addition, licorice hay is rich in proteins and is a good feed for livestock, but the root of the plant has the main healing properties. The chemical composition of the root includes malic, citric and succinic acids, beta-carotene, a large list of vitamins, as well as minerals necessary for the human body: potassium, calcium, iron, phosphorus, magnesium and others. The main biologically active substances of licorice root are triterpenoid compounds, mainly glycyrrhizic acid and flavonoids, the content of which is up to 25%. It should be noted that after processing the licorice root, that is after the extraction of glycyrrhizic acid and other biological active substances, there remains a significant amount of waste more than 80% of the feedstock (more than 100 thousand tons per year in Karakalpakstan), which is considered to be as a production waste and a liquid solution of ammonium sulfate is formed (0.5-1%) about 400 thousand tons containing a certain amount of physiological active substances. There are

many research works in the field of chemistry, technology for the production of glycyrrhizic acid and other biologically active substances from licorice root and from its waste, the creation of drugs on its basis in the literature [2-4].

In work [5], the possibility of extracting 22.9% of extractives from licorice root meal is shown as a waste of production when obtaining the drug "Licorice root syrup" at JSC "Tatkhimfarmpreparaty" Kazan. Their composition shows the presence of glycyrrhizic acid 2.76%, carbohydrates 62.49%, proteins 0.67% and amino acids 3.49%. It has been shown that the extract from licorice root meal is promising for the development of biologically active substances and medicines on its basis, since it contains such biologically active substances as glycyrrhizic acid, polysaccharides, and amino acids.

In [6], the conditions for the extraction of licorice root with ethanol were studied to maximize the extraction of triterpenoid and flavonoid compounds from it. The dependence of the yield of extractives on the extraction parameters (extractant concentration, ratio root: extractant, extraction rate and time) was determined. It was found that the highest yield of flavonoids (4.76%) and glycyrrhizic acid (0.91%) can be obtained by extraction of root by boiling with 80% ethanol at a ratio of 1: 40 in three stages, 2 hour each. It has been shown that additional grinding of root and its fractionation allows to intensify the process of extracting flavonoids and glycyrrhizic acid. Compared with the extraction of the original root from the fraction, a comparable amount of flavonoids (4.66%) and glycyrrhizic acid (0.88%) can be obtained by boiling with 80% ethanol with a reduction in the extraction time to 1 hour. With the use of instrumental thin-layer chromatography "CAMAG", the presence of up to 14 flavonoid compounds in the analyzed extracts was shown, among which liquiritigenin and formononetin predominate.

However, at present, there is no rational technology for processing licorice root waste after the extraction of the extractable substances. In spite of various methods of extraction in the licorice root, after processing, a certain amount of biologically active substances, useful microelements for the plant, remains in the waste; the bulk of the licorice root waste consists of insoluble, hardly decomposable organic substances. One of the rational ways of using root waste is to obtain organic and organic fertilizers on their basis.

In work [7], a method for obtaining a complex organomineral fertilizer from licorice waste and a technological line for its implementation is presented. According to which, in the products of two-four-year decomposition of dung and excrement of poultry, pigs and cattle, wastes of primary processing and extraction of licorice root are added and the number of pathogenic microorganisms is determined. Sterilization of fertilizer components is carried out with the distillation residue of licorice extraction and a solution of the natural bischofite mineral $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ of the sulfate type. The decomposition products of cattle manure, pig droppings and poultry excrement are disinfected with the distillation residue of the extraction of licorice root and bischofite solution with a density of 1.2-1.4 t / m³ at a rate

of 60-120; 140-180, 200-400 l / t, respectively, from the feedstock. The rates are increased by 20-40% more than the required value. Distillation residue and bischofite brine are applied to the raw materials by fine spray with continuous supply of components to the sterilizer. The saturation of organic fertilizers with macro- and microelements is carried out with ground phosphorite and recycled sludge of pickling solutions and waste of metallurgical production when the components are fed into the granulator. The disadvantage of this method is that in the process of mixing the starting materials and in the process of obtaining organomineral fertilizers, there is no chemical change in the organic substances contained in the licorice waste.

It should be noted that during the 20th century, traditional agricultural management used synthetic fertilizers and pesticides to increase crop yields. This intensive use of agrochemicals has led to a decline in biodiversity, increased irreversible soil erosion and depletion, and a significant deterioration in the quality of surface and groundwater. The need to minimize the impact on the environment without reducing yields makes it necessary to find optimal alternatives that ensure sustainable production. Research shows that the keys to sustainable agricultural production and long-term productivity of agro-ecosystems are processes that maintain soil organic matter. Soil application of organic fertilizers is a management strategy that will help counteract the progressive loss of organic matter in both the short and long term. The application of organic fertilizers improves the physicochemical, biochemical and microbiological properties of the soil and thus has a positive effect on the quality of the soil and on the indicators of plant productivity. Organic fertilizers can also promote plant health, and equivalent or even higher yields can be obtained with organic fertilizers. In this regard, interest in organic fertilizers is growing all over the world. Organic fertilizers are a constant source of nutrients due to their slow release during decomposition. By increasing the organic matter in the soil, natural fertility will be restored, which will increase the productivity of agricultural crops [8, 9].

In the study [10], acute problems such as lack of mineral fertilizers, reduced humus content and soil salinity in the cultivation of agricultural products in Uzbekistan can be solved to some extent by organizing large-scale production of organic fertilizers from organic matter of humus nature.

From the above, it can be seen that until now there is no method for converting the insoluble part of licorice root into useful products, such as humic acids, fulvic acids or humic substances necessary to increase and maintain soil fertility. Note that such studies have not been conducted for licorice root a waste of pharmaceutical production of medicinal products based on licorice root. The aim of the research is to study the processes of oxidation of licorice root waste with nitric acid to convert the insoluble organic part of licorice root into humic substances.

Object of research Uzbek-Chinese joint venture "LANEXTRAKT" Republic of Karakalpakstan, Chimbay. The root waste was air-dried and then pulverized to a particle size of 0.25 mm. After drying and grinding for analysis and research, weighed parts were taken to determine the average sample, ash

content, aqueous and alkaline solution extractable substances weighing more than 10 kg on average. The results obtained from the analysis of the original waste are presented in Table 1.

Table 1. Composition of licorice root meal

Indicator	Humidity, %	Ash content, %	Content of extractives extracted with 1% NaOH solution, %	Content of extractives recoverable by water, %	Insoluble organic matter, %
Licorice root waste	5.41	4.66	5.87	15.78	68.28

The results table 2 shows of the mass spectrometric analysis (ICP - MS) of licorice rootash. As can be seen from the table licorice root waste contains a number of trace elements necessary for plant growth and development.

Table 2 Results of mass spectrometric analysis of licorice meal ash

Name and content of elements, g/t									
Li	Be	B	Na	Mg	Al	P	K	Ca	Cr
59	1.80	16	12000	14000	80000	770	21000	65000	55
Mn	Fe	Co	Ni	Cu	Zn	Mo	Ag	Ba	Ti
1200	34000	16	40	75	100	3.30	0.490	440	3600

In order to increase the content of extractive substances, the process of oxidation of the root waste with nitric acid was studied in the licorice root waste. For oxidation 59% nitric acid produced by JSC “Maksam-Chirchik” was used. The oxidation process was carried out at concentrations of nitric acid from 20, 30 and 40%, temperatures from 30 to 60°C, duration from 30 to 120 min and weight ratio of root waste: HNO₃ from 1: 1.0 to 1: 2. It should be noted that at low concentrations and ratios, the oxidation process was low, so these data are not shown. The ratio of licorice root waste: HNO₃ meant the ratio of the organic part of the waste to nitric acid monohydrate. The experiments were carried out in a glass cylindrical reactor equipped with a thermostatic jacket and a stirrer. Acid was poured into the reactor, the preset temperature was set, the stirrer was turned on and a sample of crushed licorice root waste was loaded. At the end of the process, the reaction mass was separated into liquid and solid

phases. The solid phase was washed with distilled water from nitric acid to neutral reaction, dried to an air dry state, and the ash content, moisture content, organic matter, and the yield of extractives were determined in 1% sodium hydroxide solution. Ash content was determined according to GOST 11022-95, moisture content - according to GOST 11014-91, organic matter - according to the difference between 100 and the sum of percentages of ash and moisture.

The content of extractives of the original meal and the solid phase of the oxidized meal with nitric acid was determined as follows. The essence of which is identical to the definition of humic substances from raw materials of a humic nature. According to which a portion of the meal is placed in a conical flask A with a capacity of 250 ml, 100 ml of 1% alkaline sodium hydroxide solution is added and heated for 2 hours in a boiling water bath. After cooling to room temperature, the contents of flask A are centrifuged for 15 min at 210°C . The solution is decanted and collected in flask B. The undissolved residue is washed twice with 100 ml of sodium hydroxide solution. The suspension is centrifuged after each washing, collecting the wash solution in flask B. The contents of flask B are filtered into a 500 ml volumetric flask and made up to the mark with water. Take with a pipette 100 ml of the filtrate and transfer to a glass, then add 60 ml of hydrochloric acid there to precipitate high-molecular alkali-soluble organic acids. The suspension is centrifuged and filtered. After centrifugation, the solution is separated by decantation and the organic acid precipitate is washed with water. The precipitate is washed before the peptization of organic acids begins, which is determined by the appearance of a weak yellow color (the formation of a gel and colloid). 5 ml of hydrochloric acid are added to the colloidal solution for additional precipitation of high molecular weight organic acids.

The total precipitate of organic acids is filtered through an ashless filter, previously dried in a drying oven to constant weight at $(90\pm 5)^{\circ}\text{C}$. The filter with the organic acid precipitate is placed in a weighed weighing bottle, previously dried in a drying oven to constant weight at $(90\pm 5)^{\circ}\text{C}$. The bottle is removed from the drying oven, cooled first for 5 minutes in air, then in a desiccator with an appropriate desiccant and weighed. Control drying, cooling and weighing are carried out until the difference in mass at two successive weighings is no more than 0.001 g. Taking into account the mass of the bottle and filter, determine the mass of the sediment.

The dried filter with sediment is transferred to a weighed crucible, pre-calcined in a muffle furnace at a temperature of $(600\pm 25)^{\circ}\text{C}$ to constant weight and ashed at $(600\pm 25)^{\circ}\text{C}$ for 1-2 hours. The crucible is removed from the muffle furnace, cooled first for 5 min in air, and then in a desiccator with an appropriate desiccant and weighed. Control calcinations at the same temperature for 15 min, cooling and weighing are carried out until the difference in mass during two successive weighings does not exceed 0.001 g. Taking into account the crucible mass, determine the sediment mass.

The mass fraction of soluble organic acids (OA) in an alkaline medium and precipitated in an acidic medium in terms of dry ash-free state% is calculated by the formula:

$$OA = 100 \cdot V(m_1 - m_2) / V_1 \cdot m$$

m_1 - mass of dry OA, g;

m_2 - mass of ash OA, g;

V - total volume of the alkaline solution, ml;

V_1 - volume of an aliquot of an alkaline solution taken to precipitate OA, ml;

m - mass of a sample of meal calculated on a dry ash-free state, g, calculated by the formula:

$$m = m_3 \cdot 100 - (W + A) / 100$$

m_3 - mass of the sample of the meal, g;

W - mass fraction of analytical moisture in the meal, %;

A - ash content of the analytical meal sample, %.

The dry and ash-free organic part of the liquid and solid phase is oxidized meal. Its determination was carried out according to the method described in [11]. The yield of oxidized meal was calculated for the organic matter of the original meal.

The solid phase of the oxidized meal after the separation of alkali-soluble organic substances from it is the residual meal. It was thoroughly washed with distilled water, then dried to constant weight, and the yield of oxidized meal on the organic mass was determined. The difference between the amounts of organic matter in the solid phase and residual meal gives us the content of extractives in 1% NaOH solution in oxidized meal.

Also, nitrogen oxides released during the oxidation of meal with nitric acid have been determined. Using a water-jet pump, they were passed through absorbers with 0.5 N NaOH solution. All solutions were collected together, brought to the mark of 500 ml, from which an aliquot was taken for the determination of nitrogen according to Kjeldahl [12].

It is known that the reactivity and multifunctionality of high molecular weight organic acids depends on the content of various oxygen-containing groups. The presence of these groups, on the one hand, provides the cation-exchange properties of organic acids, and on the other hand, makes its surface more hydrophilic. To determine the total content of phenolic and carboxyl groups of high molecular weight organic acids isolated from oxidized meal with a fraction of 0-0.25 mm, a sample of 0.5 g is taken with an accuracy of 0.0002 g. 50 ml of 0.1N NaOH solution is poured into the OA sample and left to interact for a day with periodic shaking. Then the solid phase is separated on a paper filter. An aliquot is taken from the filtered solution, transferred to a conical flask for titration and titrated with 0.1N HCl solution in the presence of phenolphthalein indicator until the raspberry color is discolored. In

parallel, a blank experiment is carried out without OA. The sum of acidic groups (OH + COOH) in mg - eq/g is determined by the formula:

$$N_{(OH+COOH)} = ((V - V_2) V_3 N_{HCl}) / (GV_2)$$

where V is the volume of HCl used to titrate the control solution, V_1 is the volume of HCl used to titrate the solution with OA, ml; V_2 — volume of the aliquot, ml; V_3 is the volume of 0.1N NaOH solution added to the sample used, ml; N_{HCl} is the normality of the HCl solution; G - weight of the sample OA, g.

The method for determining carboxyl groups is similar to determining the content of acidic groups. Add ml of 0.1N $NaHCO_3$ solution to a sample of OA 0.5 g and leave for a day. The solution is filtered off. An aliquot of the filtrate is titrated with 0.1 N HCl solution in the presence of methyl orange indicator until the yellow color turns to raspberry. The calculation of the concentration of carboxyl groups in OC is carried out in the same way as described above. The content of phenolic hydroxyls is calculated from the difference in the total content of acidic and carboxyl groups. To determine the content of carbonyl groups 50 ml of a 0.1N solution of hydroxylamine hydrochloric acid is added to a sample of OA 0.5 g, stirred and left for a day. The solution is filtered off. An aliquot is taken from the filtrate and titrated with 0.1N NaOH solution in the presence of phenolphthalein until a stable crimson color of the solution appears. The calculation of the number of carbonyl groups is carried out according to the formula:

$$N_{C=O} = ((V - V_1) V_3 N_{NaOH}) / (GV_2)$$

where V is the volume of NaOH used for titration of the control solution ml; $V_1 - V_{(NaOH)}$ used for titration of the solution with OA, ml; V_2 - volume of the aliquot, ml; V_3 - volume of 0.1N $NH_2OH \cdot HCl$ solution added to the test portion, ml; N_{NaOH} - normality of NaOH solution; G - weight of the sample OA, g.

The experimental results are shown in tables 2-6. On table 3 shows how the composition of the oxidized waste changes depending on the concentration and rate of nitric acid. The amount of oxidized waste increases to 118.2% in relation to the organic part of the original root waste. At a HNO_3 concentration of 20%, a root waste: HNO_3 ratio of 1 : 1.6, a temperature of 40°C and a duration of 2 hours, 45.37% of the original root waste remains under-oxidized. The main purpose of oxidation is to increase the content of alkaline-soluble organic acids in the waste, while being successfully achieved from 5.87% in the original waste to 49.28% in the oxidized waste. Relatively small (4.21%), with the above process parameters, the loss of nitrogen into the gas phase.

Table 3 The productivity of the oxidation products of the root waste (in% to the organic part of the oxidized waste), depending on the norm and concentration of nitric acid (τ - 120 minutes, t - 40°C)

Oxidation	Consentrati	Root waste ratio: HNO_3
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products	on HNO ₃ , %	1 : 1.0	1 : 1.2	1 : 1.4	1 : 1.6	1 : 1.8	1 : 2
Oxidized waste	20	102.3	103.5	104.3	105.2	106.2	107.1
	30	105.1	106.4	107.5	108.7	110.8	112.7
	40	106.6	107.3	109.7	110.7	114.7	118.2
Extractive substances 1% NaOH solution	20	47.33	48.39	48.08	49.68	49.81	49.94
	30	48.17	49.15	48.56	50.50	51.01	52.37
	40	49.59	49.79	51.04	51.07	52.55	53.17
Organic acids precipitated in an acidic environment	20	14.23	13.29	11.15	10.80	9.80	8.81
	30	12.79	11.63	10.40	9.95	8.34	7.62
	40	11.52	10.17	9.80	9.38	7.08	6.98
Water- soluble organic matter	20	2.22	3.35	4.09	4.95	5.31	6.60
	30	3.91	5.12	6.84	6.03	6.75	7.30
	40	6.19	6.77	7.64	8.45	8.79	10.39
Residual waste	20	50.45	48.26	47.83	45.37	44.88	43.46
	30	47.92	45.73	44.60	43.47	42.24	40.33
	40	44.22	43.44	41.32	40.48	38.66	36.44
Losses of nitrogen oxides (NO, NO ₂). in terms of nitrogen	20	6.1	5.97	4.45	4.21	3.75	3.21
	30	10.7	8.79	7.32	6.75	5.36	4.97
	40	15.94	13.22	12.31	11.7	10.54	9.82

Table 4 shows the change in the composition of the oxidized waste at HNO₃ concentrations of 20 and 30%, the ratio of waste: HNO₃ = 1: 1.6, depending on the temperature. Optimum oxidation parameters are observed at 40°C. At this temperature, we have the maximum amount of oxidized root waste and the highest content of extractives in it (48.50 and 49.60%).

Table 4 The yield of oxidation products of licorice root waste depending on the temperature of the oxidation process

Temper	Determined components in% to organic part
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ature of the process	Oxidized waste	Extractive substances 1% NaOH solution	Organic acids precipitated in an acidic medium	Water-soluble organic matter	Residual waste	Losses of nitrogen oxides (NO. NO ₂). in terms of nitrogen
Concentration HNO ₃ = 20%. proportion. waste : HNO ₃ = 1 : 1.6. τ - 75 minutes						
30	104.3	46.19	7.93	1.76	52.05	3.12
40	105.2	49.68	10.80	4.95	45.37	4.21
50	102.4	52.28	8.82	8.56	39.16	7.84
60	93.5	54.74	6.28	12.65	32.61	12.54
Concentration HNO ₃ = 30%. coot. waste : HNO ₃ = 1 : 1.6. τ - 60 minutes						
30	102.3	46.61	7.68	3.45	49.94	5.65
40	108.7	50.50	9.95	6.03	43.47	6.75
50	105.8	49.58	8.54	12.05	38.37	12.68
60	101.2	48.41	7.03	24.24	27.35	18.54

Table 5 shows the yield of oxidation products at a waste: HNO₃ ratio = 1 : 1.6, a temperature of 40°C and HNO₃ concentration of 30 and 40%, depending on the duration of the interaction of waste with nitric acid. It can be seen from this table that at a concentration of HNO₃ = 20%, the maximum content of humic acids in oxidized waste can be achieved with a 75 minute interaction. By further increasing the duration of the oxidation process, we thereby increase only the loss of nitrogen oxides into the gas phase.

Table 5 Yield of oxidation products of licorice root waste depending on the duration of the oxidation process

Oxidation time. min	Determined components in% to organic part					
	Oxidized waste	Extractive substances 1% NaOH solution	Organic acids precipitated in an acidic environment	Water-soluble organic matter	Residual waste	Losses of nitrogen oxides (NO. NO ₂). in terms of nitrogen
concentration HNO ₃ = 20%. proportionmeal : HNO ₃ = 1:1.6. temperature 40°C						
30	97.3	39.79	8.93	1.16	59.05	1.76
45	101.5	42.97	9.38	2.24	54.79	2.39
60	103.4	46.86	10.22	3.86	49.28	3.74

75	105.2	49.68	10.80	4.95	45.37	4.21
90	101.4	48.54	10.08	9.65	41.81	6.84
120	99.8	42.55	9.01	19.04	38.41	10.54
Concentration						
HNO ₃ = 30%. Proportion meal : HNO ₃ = 1:1.6. температура 40°C						
25	98.3	41.25	9.06	3.04	55.71	2.88
40	101.4	44.52	9.34	4.23	51.25	4.81
50	104.8	47.25	9.67	5.36	47.39	6.21
60	108.7	50.50	9.95	6.03	43.47	6.75
80	105.8	49.19	10.44	11.95	38.86	9.84
120	102.4	47.84	9.96	19.14	33.02	14.45

Table 6 shows that, as a result of the oxidation of licorice root waste in the latter, the content of active functional groups increases, both in the oxidized waste itself and in its organic acids. If in the initial waste the content of the carboxyl group was 2.56 mg-eq/g, and the phenolic hydroxyl content was 3.19 mg-eq/g, then in the oxidized waste these figures increased to 3.4 mg-eq/g and 5.01 mg-eq/g, respectively, and in organic acids up to 5.02 mg-eq/g and 5.64 mg-eq/g.

Table 6 Active functional groups of the original licorice root waste and its oxidation products

Substances	Humidity, %	Ash, %	Functional groups		
			COOH+OH, mg-eq/g	COOH mg-eq/g	OH mg-eq/g
Original licorice rootwaste	5.41	4.66	5.75	2.56	3.19
Oxidized waste	4.60	1.18	8.41	3.4	5.01
Organic acids precipitated in an acidic medium of the original waste	2.01	0.69	9.79	5.0	4.79
Organic acids precipitated in an acidic medium of oxidized waste	3.83	0.63	10.66	5.02	5.64
Residual organic matter of the original waste	5.34	6.04	2.53	1.18	1.35
Residual organic matter oxidized waste	5.11	6.76	2.99	1.18	1.81

Thus, the study showed that the oxidation of licorice root waste with nitric acid increases the content of extractive substances, which is a valuable product for obtaining organic and organomineral fertilizers, as well as plant growth stimulators.

Gratitudes

The study was carried out using the root of the liquorice root waste of the Uzbek-Chinese JV "LANEXTRAKT", Republic of Karakalpakstan, Chimbay.

Conflict of interests

The authors declare that they have no conflicts of interest requiring disclosure in this article.

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