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DESCRIPTION OF HYDROLYTIC LIGNIN IN TERMS OF ITS USE AS FERTILIZER AND AMENDMENT

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Abstract

The paper describes the chemical and physical composition, as well as, the properties of the waste-hydrolytic lignin from biochemical plants, which possesses fertilizing potential and whose object of activity is to produce fodder yeast. The properties of the latter, to be used as fertilizer and amendment for the restoration of the fertility of low productivity soils, are argued.

Key words: *waste, hydrolytic lignin, biochemical plants, chemical composition, physical composition.*

INTRODUCTION

Hydrolytic lignin is not usually used for psychological, economic, legal, as well as technological reasons. Being accumulated as waste year by year, it affects the normal functioning of the soil, of the atmosphere, and of water resources. However hydrolytic lignin contains biophile elements necessary for the plants. By virtue of maintaining a reasonable balance of soil elements, it is imperative to recuperate and to reintegrate it into the agricultural circuit through transforming and using it as fertilizer and amendment. By augmenting the hydrolytic lignin, three stringent current social-economic issues will be simultaneously solved: restoration of agricultural soil fertility, increase of plant productivity, and protection of the environment from pollution with organic wastes.

The aim of the paper is to present an analysis of chemical and physical properties of the hydrolytic lignin in terms of its being used as fertilizer and amendment.

MATERIAL AND METHOD

Samples of hydrolytic lignin, collected from dumps of biochemical plants from the cities Balti and Tighina, Republic of Moldova, during the period 1980-2005, served as material for analysis. The applied research methods include those of synthesis, generalization and data processing. Statistical data processing was performed according to the statistical methods using MS Excel programmer.

RESULTS AND DISCUSSIONS

The activity of the biochemical plants consists in producing fodder yeast. The sugars (carbohydrates) from various wastes of plant origin: wood shavings, saw dust, corn cobs, husks of seeds, etc., serve as nutritional source for the yeast. Carbohydrate hydrolysis is performed by treatment with sulphuric acid of 0.5 to 1.0% on raw material at a temperature of 140-190°C and the pressure of 0.4 to 1.2 Mpa [1, 2].

In these conditions, about 10-20% of the original raw material is dissolved and placed in the hydrolysis tower. The substances which were not dissolved (actual lignin and some polysaccharides) are downloaded from the tower as waste under the name of hydrolytic lignin.

The hydrolytic lignin is a dark brown solid material. Being downloaded from the hydrolysis tower, it retains, to a great extent, its form and raw material particle size, because the latter is hydrolyzed in a small proportion of up to 20% of the initial raw

material introduced into the tower [3, 4]. According to its chemical composition, the hydrolytic lignin consists of a complex of substances, whose mass is composed of natural lignin and poly-saccharine (84-91% of the dry mass of hydrolytic lignin). There are also present, various organic acids, sulphuric acid, minerals. Simultaneously, it contains a significant amount of functional groups: carboxyl (5-6%), hydroxyl (6-8%), methoxyl (10-11%), acid (9-14%) and phenol (3%) [5]. The presence of these functional groups renders an active role to the hydrolytic lignin in the chemical reactions.

Hydrolytic lignin possesses a strongly acid reaction (Table 1). The hydrolytic acidity is also extremely high, with a maximum of 1017 me H/100 g of dry mass. The average humidity (X) is of 63.7% with a very small standard deviation (S) (5.28%). The dry mass of hydrolytic lignin consists of up to 87.8% of organic matter. According to statistics, this value is very stable; the coefficient of variation (V) does not exceed 6%.

Therefore, the C:N proportion is very high (89-138); it is ten times higher than the optimum, when the activity of micro organisms does not affect the plant needs in nitrogen. Mineral nitrogen is presented in small amounts (0.4 to 4.0 mg/100 g). The quantities, which characterize the hydrolysable nitrogen - nitrogen potentially available for plants, are higher. The amount of easily and difficultly hydrolysable nitrogen is equal to an average of 100 mg/100 g of dry mass.

The ash varies within 2.9 to 18.6 %. The predominant mineral elements are: silicon (6.09%), sulphur (1.26%), calcium (0.96%). Total phosphorus constitutes an average of 0.20% with a standard deviation of 0.04%. The potassium content is not high either (0.60%), which is also characteristic of traditional organic fertilizers [6].

Out of the list of main microelements, hydrolytic lignin practically misses only cobalt. Molybdenum (0.1 to 0.7 mg/kg) and boron (1-4mg/kg) are found in small quantities. Concentrations higher than 18-90mg/kg are characteristic of manganese, copper and zinc.

Table 1. Chemical composition of hydrolytic lignin related to dry mass (n=15)

Indices and the measure unit	x	min	max	S	v
pH (H_2O)	3.5	1,9	5,9	1,22	35
Hydrolytic acidity, meH/100 g soil	796	510	1017	167.1	21
Humidity, %	63.7	59.1	76,3	5.25	8
Organic matter, %	87.8	81.4	97.1	5.24	6
Natural lignin, %	42.1	29.4	52.8	3.79	9
total C, %	47.6	41.3	51.4	3.49	7
Huminic acid C, %	4.5	3.2	6.8	1.39	31
fulvic acid C, %	5.1	3.5	7.9	1.74	34
Huminic acid C : fulvic acid C	0.9	0.5	1.5	0.25	28
total N, %	0.42	0,3	0.58	0.09	21
total C : total N	116	89	138	16.5	14
N-NO_3, mg/100 g soil	0.4	0.1	0.7	0.27	67
N-NH_4, mg/100 g soil	4.0	2.0	8.0	2.21	55
Easily hydrolysable N, mg/100 g soil	58.0	39.6	78.6	5.22	9
Difficultly hydrolysable N, mg/100 g soil	40.0	37.6	42.6	2.40	6
P_2O_5 total, %	0.2	0.15	0.25	0.04	18
Accessible P_2O_5, mg/100 g soil	10.2	2.3	19.8	7.09	69
K_2O total, %	0.6	0.04	2.11	0.67	111
Accessible K_2O, mg/100 g soil	26.9	16.4	34.6	7.20	27
total SiO_2, %	6.1	3.0	11.5	3.06	50
total Al_2O_3, %	0.12	0.06	0.19	0.04	34
total Fe_2O_3, %	0.37	0.2	0.62	0.31	71
total CaO, %	0.96	0.84	1.12	0.09	9
MgO total, %	0.15	0.11	0.19	0.02	16
total SO_3, %	1.26	0.7	2.01	0.47	37
total Na_2O, %	0.02	0.01	0.04	0.01	45
total Mn, mg/kg	86	11	183	66.4	77
total Cu, mg/kg	90	32	152	49.3	55
total Zn, mg/kg	18	3	65	18.4	102
total B, mg/kg	2	1	4	1.05	53
total Mo, mg/kg	0,3	0.1	0.7	0.23	56
total Cd, mg/kg	0	-	-	-	-
total Pb, mg/kg	2	1	3	0.82	41
total Ni, mg/kg	8	2	12	3.37	42
total Co, mg/kg	0	-	-	-	-

Approximately 50% of organic matter is natural lignin. From the range of organic fertilizers and of other fertilizing materials, hydrolytic lignin is the richest in organic matter (peat close) and also the poorest in total nitrogen (0.30 to 0.58%).

The fact that these elements are in comparatively large quantities can be considered positive, as they are assimilated by plants more intensely and are often observed in the soil in minimal amounts. Metal shaving a direct toxic effect are present in very low amounts (lead, 1-3 mg/kg) or are altogether absent (cadmium). Calcium predominates among aqueous extract ions and forms 8.3 ml, magnesium, and sulphur 3.2 ml, 11.9 ml/100 g of dry lignin correspondingly (Table 2).

Table 2. Chemical composition of aqueous extract of hydrolytic lignin, me/100 g dry mass (n=15)

Indices	x	min	max	S	v
Dry residue, %	4.59	1.45	9.78	3.04	66
Mineral residue, %	0.92	0.64	1.34	0.24	26
Carbon, %	0.9	0.5	1.50	0.32	37
Ca^{2+}	8.3	5.3	12.2	2.85	34
Mg^{2+}	3.2	0.7	5.2	1.65	51
Na^{+}	0.6	0.2	0.9	0.23	40
K^{+}	1.3	0.4	2.2	0.63	48
NH_4^{+}	0.4	0.2	0.7	0.16	38
HCO_3^{-}	1.6	0.1	3.8	1.33	82
SO_4^{2-}	11.9	7.1	17.4	3.33	27
Cl^{-}	0.06	0.04	0.10	0.02	35
H_2PO_4	0.2	0.03	0.3	0.09	45
NO_3	0.08	0.06	0.1	0.01	18

Based on these indices, it can be inferred that, among the water soluble minerals, calcium sulphate predominates in lignin - the substance that gives it an ameliorative character. And as it results from the difference of total residue value and of the mineral one, 80% of water soluble substances are organic constituents. Therefore, an essential part of the lignin mass consists of water - soluble substances, i.e. it is active from the chemical and mineralogical points of view.

The physical properties of hydrolytic lignin are very interesting under the agronomic aspect. The contents of a lignin fraction smaller than 0.001 mm does not exceed 11.4% (Table 3).The fractions bigger than 0.001-0.05 mm (the sand and the dust) constitute together 90 % of the lignin mass. From the granule-metric point of view, the hydrolytic lignin is characterized as a mineral possessing a coarse texture, falling within the average clay-sand subclass [7].

The micro structural composition analysis showed that 64-74 % of the fractions smaller than 0.01 mm were of the sand size. Consequently, while the analysis of size fractions from 0.01 to 0.005 mm, 0.005 to 0.001mm and less showed that they averaged 10.4%, 12.9% and 9.9%, the micro structural analysis of these fractions averaged 4.2%, 3.3% and 6.4%.

So, they considerably decreased, increasing the share of fractions from 0.25 to 0.05 mm from 28.6% (granule-metric analysis) to 49.5%. Under natural conditions, the hydrolytic lignin is not artificially dispersed with chemicals, as it is done in the case of particle size analysis; it is a sandy material in terms of micro structural composition.

Table 3. Physical properties of dry mass hydrolytic lignin (n=15)

Indices	x	min	max	S	v
Granulometric fractions					
1.00-0.25 mm	16.6	14.3	18.2	1.48	9
0.25-0.05 mm	28.6	25.3	31.9	2.28	8
0.05-0.01 mm	21.6	18.6	24.1	1.86	9
0,01-0.005 mm	10.4	8.5	12.4	1.38	13
0.005-0.001 mm	12.9	10.5	15.1	1.60	12
<0.001 mm	9.9	7.3	11.4	1.31	13
<0.01 mm	33.2	29.7	36.3	2.23	7
Microstructures fractions					
1.00-0.25 mm	15.6	13.8	17.1	1.14	7
0.25-0.05 mm	49.5	46.8	52.4	1.90	4
0.05-0.01 mm	21.0	18.1	23.8	2.06	10
0.01-0.005 mm	4.2	3.5	5.1	0.57	13
0.005-0.001 mm	3.3	2.8	4.0	0.44	13
<0.001 mm	6.4	5.1	6.5	0.86	13
<0.01 mm	13.8	12.1	15.4	1.08	8
Hydroscopic coefficient, %	5.97	5.53	6.53	0.42	7
Density, g/cm^3	1.37	1.27	1.45	0.06	5
Apparent density, g/cm^3	0.23	0.15	0.27	0.04	13
Total porosity, %	83	81	88	2.06	3

Such composition may have favorable consequences for agricultural practices. Being incorporated into the soil, the hydrolytic lignin will keep the soil in a loose state, more permeable to water and air.

The potential favorable consequences of hydrolytic lignin for agriculture are also confirmed by other physical properties. The density of lignin is very low (1.27-1.45 g/cm^3). The lignin apparent density (0.15-0.27 g/cm^3) is also characterized by very low parameters. While the low density is explained by the fact that 90 % of the lignin composition is formed of organic matter, the apparent density is caused by the high porosity of the hydrolytic lignin (81-88%).

The apparent density is two-three times lower than that of manure. The same volume of lignin will weigh two-three times less than the same volume of manure.

The low density, the high porosity, and as a result, the high water absorption capacity (210-450%) offer to lignin the perspective not only as an agricultural fertilizer, but also as a sub-layer in greenhouses and in other protected spaces. The material possessing such characteristics can serve as a good reservoir both for the water and air, as well as for nutritive elements.

CONCLUSIONS

1. Hydrolytic lignin possesses a powerful acid reaction (pH=3.5) and hydrolytic acidity (796 meH/100 g of dry mass). The average humidity constitutes 73.7%. It is rich in organic substances (87.8%) and poor in total nitrogen (0.42%), which determines the especially high value of the proportion C:N (116).
2. Among the mineral water soluble substances, calcium sulphate predominates in hydrolytic lignin; the substance renders to lignin an ameliorative character. Around 80% of water soluble substances are formed of organic constituents, which are active from the chemical and mineralogical points of view.
3. From the physical point of view, hydrolytic lignin is characterized as a sandy material. Being incorporated into the soil, it will maintain it in a loose state that will be more permeable to water and air.
4. The hydrolytic lignin possesses a density of 1.27-1.45 g/cm^3 and a reduced apparent density of 0.15-0.27 g/cm^3. Its porosity is of 83% and has high water absorption capacity of 210-450%. These parameters offer to the hydrolytic lignin the perspective of not only a fertilizer for agriculture, but also for being used as a sub-layer in greenhouses and in other protected spaces; it can serve as a good reservoir not only for water and air, but also for nutritive elements.

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