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TÍTULO: Propiedades fisicoquímicas del abono de aves de corral Fertilizante del pirólisis sólido.

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RESUMEN: En este documento consideramos la posibilidad de utilizar un producto de pirólisis sólida de estiércol de aves de corral como potencial fertilizante y mejorador de la estructura del suelo para fines agrícolas. Los resultados mostraron que se estudió la composición granulométrica de productos sólidos de pirólisis, humedad y fracción de masa de ceniza y densidad aparente. Se estudian los parámetros del extracto de agua. El contenido de iones de metales pesados se determinó mediante el método de espectroscopia de absorción atómica. Por cromatografía iónica se determinó el contenido de residuos ácidos en el extracto acuoso. La demanda biológica de oxígeno (DBO) se investigó mediante el método yodométrico.

PALABRAS CLAVES: productos de pirólisis, estiércol de aves, fertilizante, suelo.

TITLE: Poultry manure physicochemical properties Fertilizer from Solid Pyrolysis.

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ABSTRACT: In this paper, we consider the possibility of using a solid pyrolysis product of litter poultry manure as a potential fertilizer and soil structure improver for agricultural purposes. he results showed that the granulometric composition of solid pyrolysis products, humidity, and mass fraction of ash and bulk density were studied. The parameters of water extract are studied. The content of heavy metals ions was determined by the method of atomic absorption spectroscopy. By ion chromatography the content of acidic residues in the aqueous extract were determined. The biological oxygen demand (BOD) was investigated by the Iodometric method.

KEY WORDS: pyrolysis products, poultry manure, fertilizer, soil.

INTRODUCTION.

One of the priority directions of development of Russia are branches of agriculture to which today the country leaders began to draw close attention (Ivanov, Belov, 2017). The agro-industrial complex for national economy is extremely important from the point of view of ensuring food security. Development of the country is impossible without agro-industrial complex. So, within import substitution, production of some types of agricultural products steadily grows in the Russian Federation. It is possible to predict that the role of agro-industrial complex in economy of Russia in the next years will only amplify.

In the area of animal husbandry, agricultural production has different structural components. In particular, the issue of integrated development of natural production in the livestock sector arises. In the production of meat and milk products, a large amount of waste in the form of manure is produced annually in Russia, and so on.

Poultry meat production is developing particularly fast. It is known that the production of eggs and meat of birds creates environmental problems related to the large volume of poultry manure, which is one of the most important environmental problems in the production of poultry products. In this case it is a question of a sanitary-dangerous object, since the poultry manure are considered as toxic wastes of production of the III hazard class, which requires conducting in-depth studies in the direction of its processing. The existing processing technologies do not ensure the proper level of utilization of poultry manure, in connection with which, a large amount of decomposing material accumulates in the adjacent territories.

The analysis of information and technologies for the utilization of poultry manure (Yu, Averyanov, 2010; Yu, et al. 2015; Lubov, 2004; Jebaseeli and Dhayabaran, 2013). showed that pyrolysis should be considered as a promising and most effective method of utilizing poultry manure. With pyrolysis, thermal energy can be used for technological needs. Solid sorbents from wastes are formed together with other products - gaseous and liquid pyrolysis fuel, due to which the autonomous operation of the recycling complex is possible.

DEVELOPMENT.

Methods.

Stirring of solutions was carried out on the LAB-PU-02 shaker. Mass measurement was carried out laboratory scales Ohays RV 512 and analytical scales RV 214. The ionomer ANION 4100 was applied to measurement of pH value of solutions. Mixing of the solutions was carried out on the LAB-PU-02 shaker.

To determine the bulk density, the test samples were placed in a previously weighed cylinder of 20 ml volume and the volume occupied by the coal before and after shaking was measured. Shaking time - 1 minute (Ilnar, et al. 2017).

The distribution of solid pyrolysis particles of poultry manure by size, was determined with the help of the sieve analysis and laser particle size analyzer “Microsizer 201C”.

The moisture content of solid pyrolysis products was determined using a moisture analyzer “ML-50”, in which the principle of thermogravimetric analysis was realized (Ilnar, et al. 2016). In this analysis, the sample is dried with a halogen lamp and the moisture content (%) is calculated on the basis of the difference between wet and dry weight.

The mass fraction of ash (mineral part of the residue) was determined as the ratio of the mineral impurities mass, after calcination of the residual and bringing it to a constant mass, to the mass of dry sample, taken for analysis. The mass of the dried sample was in the range (1-2.5g).

Determination of water extract parameters was carried out as follows: 30 g samples, weighed with an error of not more than 0.1 g, were placed in conical flasks. The samples were poured with 150 cm^3 of distilled water by a cylinder. The sorbent with water was stirred for 30 minutes on a shaker and allowed to settle for 10 minutes. This mass was filtered with the help of "blue tape" filters. The first portion of the filtrate, up to 10 cm^3, was discarded and only then the filtrate was collected into a clean dry receiver. Turbid filtrates were re-filtered with membrane filters "nylon" (Ilnar, et al. 2016).

The content of anions and cations in the aqueous extract of carbon-containing pyrolysis products was discarded by ion chromatography using a liquid chromatograph "Stayer". The principle of operation of the chromatograph is based on the separation of the analyzed mixture in a chromatographic column and the subsequent measurement of the content of the sample components by a conductometric detector.

Determination of the content of heavy metal ions was carried out by atomic-emission spectrometry with inductively coupled plasma on a spectrometer Agilent 720-OES.

Results and discussion.

As samples of the product of pyrolysis processing of carbon-containing wastes, obtained at the installation of low-temperature pyrolysis of the complex for processing sludge deposits by the method of continuous pyrolysis. The poultry manure was subjected to pyrolysis processing. The solid product of pyrolysis of poultry manure is a powder of gray-black color heterogeneous in composition with foreign inclusions in the form of sawdust (substrate) with a sharp odor.

The primary indicators of the solid product of pyrolysis of chicken manure are bulk density, moisture, mass fraction of ash and granulometric composition. The obtained results of determination of bulk density, moisture content, ash content and granulometric composition are presented in tables 1,2 and 3.

Table 1. General characteristics of solid pyrolysis product

Sample	Bulk density, g/dm^3	Moisture, %	Mass fraction of ash (A),%
solid pyrolysis product of poultry manure	560.3	2.25	50.3
standard for the activated charcoal	240*	10**	10**
standard for a poultry manure	-	no more 40***	not less 15***

*** GOST 6217-74 "Coal active wood crushed".**
**** GOST 4453-74 "Coal the active clarifying wood powdery. Specifications".**
***** GOST P 53765-2009 "Poultry manure. Raw materials for production of organic fertilizers Specifications".**

For moisture and ash content, the solid product of pyrolysis of poultry manure does not contradict GOST. The average value of two parallel determinations of bulk density was 560.3 g / l at the normative value according to GOST "Coal active wood crushed" - 240 g / l. The increased density

of the solid product of pyrolysis is a consequence of its increased ash content due to the presence of litter mineral components, possibly soil or clay inclusions in the original poultry manure.

Table 2. Particle size distribution for pyrolysis products (%).

Particle size, μm	Content, %
<1	0.45
1-10	10.9
10-100	52.1
100-200	27.6
200-500	8.35
> 500	0.65

The distribution of the sample of the solid pyrolysis product is close to normal. Particles with a size of 10-100 μm prevail in the sample, which is satisfactory from the point of view of practical use in terms of introducing material into the soil.

The specific electrical conductivity and mineralization of the aqueous extract were measured in order to determine the mobile macro minerals that can readily pass into the soil cover when a solid pyrolysis product is introduced into the soil. The method of analysis is conductometric. The value of the hydrogen index of aqueous extract was also determined by the pH study method.

The results of the study of pyrolysis products aqueous extract of carbonaceous wastes are presented in Table 3.

Table 3. Indices of aqueous extract of pyrolysis products.

Sample	Mineralization, mg/l	Specific electrical conductivity (SEC), μS/cm	pH, unit pH
Solid pyrolysis product of poultry manure	5290	9830	5.90
BAU	55.2	115.6	7.38
Standard for a poultry manure	-	-	6.8-8.0

For comparison, Table 3 shows the water extract parameters for BAU and poultry manure. The pH of the aqueous extract of a solid pyrolysis product responds in practice to the pH of tap water, where the weak acidity is due to the dissolution of carbon dioxide in the water. In principle, the pH can be increased to a value of 6.8 by some increase in the pyrolysis temperature or by another readily available method. For example, by adding a small amount of KOH or ammonia water.

The relatively high mineralization value indicates a possible emission from the solid product of pyrolysis into the aqueous phase of macro- and microelements.

The content of anions and cations in the aqueous extract was determined by ion chromatography (device-chromatograph ionic liquid grade "Stayer"). The results are shown in Table 4 and 5.

Table 4. Content of anions

Sample	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Solid pyrolysis product of poultry manure, mg/dm^3 (in a water extract after extraction by water for 20 min.)	2158	20.4	38.8	1616.7	2590.1
BAU, mg/dm^3	9.69	4.88	1.95	0.215	7.49
PDK, mg/dm^3	1000	-	-	-	1000
Solid pyrolysis product of poultry manure, g/kg (the content in the solid product of the water-soluble form of the ingredient according to the data in the aqueous extract after extraction by water for 20 min.)	10.8	0.10	0.19	8.1	13
Standard for a poultry manure, g/kg	-	-	-	8.0	-

It is important that according to phosphate ions (the most important component of manure as a fertilizer), the solid product of pyrolysis meets the norms of poultry manure.

Table 5. Content of cations.

Sample	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Solid pyrolysis product of poultry manure, mg/dm^3 (in a water extract after extraction by water for 20 min.)	298.2	1051.7	2379.5	629.1	584.9
BAU, mg/dm^3	0.611	11.8	23.1	2.26	23.4
PDK, mg/dm^3	-	200	-	-	-
Solid pyrolysis product of poultry manure, g/kg (the content in the solid product of the water-soluble form of the ingredient according to the data in the aqueous extract after extraction by water for 20 min.)	1.49	5.26	11.9	3.15	2.92
Standard for a poultry manure, g/kg	25	-	6	-	-

According to potassium, a significant macroelement, the solid product of pyrolysis is twice as high as the norm of the poultry manure itself with litter. But magnesium is more than a hundred times in the litter itself (Table 1). Calcium is 7.5 times less than in the original poultry manure. The hardness was 78.6 meq / l.

The content of heavy metal ions in aqueous extract was determined by the method of atomic emission spectroscopy (Alekseeva, et al. 2016; Fazullin, Mavrin, Melkolvan, 2014). Microelements in the composition of fertilizers for plants include boron, copper, iron, manganese, molybdenum, zinc.

The introduction of fertilizer for feeding the soil with microelements is an activity that depends on the type of soils, the reaction of the soil solution, the content of microelements in the soil itself, and so on. Therefore, in this paper we confine ourselves to the fact of detecting and quantitatively taking into account some trace elements and toxic heavy metals in the aqueous drawing of a solid pyrolysis product of poultry manure for litter in mobile form.

The content of heavy metal ions in the aqueous extract of the solid pyrolysis product of the poultry manure and the content in the solid product itself and some of the regulatory indices are given in tables 6 and 7.

Table 6. The content of heavy metal ions in aqueous extract.

Sample	Concentration, mg/dm^3						
	Al	Pb	Fe	Mn	Cu	Cr	Zn
Solid pyrolysis product of poultry manure	122.5	14.1	<0.001	10.5	1,94	<0.001	<0.001
BAU	-	-	0.013	0.039	0.006	0.009	0.021

It is established (Table 6) that the emission into the aqueous phase of heavy metals from the solid pyrolysis product is several times higher than the normative indices for wastewater, as well as hundreds of times higher in comparison with the emission from commodity sorbents of the BAU type.

Table 7. The content of the water-soluble form of heavy metals in the solid pyrolysis product of poultry manure

Sample	Concentration, mg/kg			
	Al	Pb	Mn	Cu
Solid pyrolysis product of poultry manure	612.5	70.5	52.5	9.70
The maximum permissible content of heavy metals in sewage sludge used for fertilizers (in mg / kg dry matter)	-	500	-	1500
Regional background content specifications heavy metals in the soils of the Republic of Tatarstan (mobile form), mg / kg	-	2	570	0.4

With the interpretation of data on the content of heavy metals in a solid pyrolysis product, the situation is not unique, since there is no certainty with the normalization of heavy metals in relation to this situation. On the one hand, the content of heavy metals in a solid pyrolysis product is

significantly less than in sewage sludge used as fertilizer, and on the other hand, for lead and copper (microelement) - significantly exceed the background content of these metals in the soils of the Republic of Tatarstan. Nevertheless, the fact of the presence of a number of trace elements in the solid pyrolysis product can be considered established. More definite conclusions can be drawn after additional measurements.

In general, it can be noted that at this stage, it is not appropriate to activate a solid pyrolysis product, for example alkali solutions, for possible use as a sorbent because of the high content of a number of ingredients that are subject to emission into the aqueous phase. Before it is necessary to receive a product of pyrolysis of a poultry manure covering at more high temperature for fuller decomposition of a number of his components.

The biochemical oxygen demand (BOD) was determined by a standard procedure (Fazullin, Mavrin, Sokolov, 2014; de Paulo Lobato, 2018).

Table 7. The biochemical oxygen demand

Sample	BOD_5, mgO2 / dm3
Solid pyrolysis product of poultry manure	136.5
BAU	41.7
PDK	300

According to the standard for wastewater, the solid pyrolysis product has a satisfactory BOD5 value. It is possible to tolerate a relatively low level of organic substances and other substances that are easily oxidized by oxygen.

Summary.

The method of low-temperature continuous pyrolysis of poultry manure for litter produced a solid product – semi-coke as a potential fertilizer.

At a bulk density of 560 g / dm3 and a moisture content of 2.3%, the semi-coke of gray-black color was distinguished by high ash content (more than 50%) and granulometric composition with more than 50% content of particles within 10-100 μm.

The water extract of carbonizate was characterized by high electrical conductivity and mineralization and a pH value of 5.9.

According to the content in the water extract, carbonizate exceeds birch charcoal, activated by water-soluble phosphates by 7500 times, nitrates by 20 times, sulfates by 350 times, chlorides by 220 times, by ammonium cations by 490 times, by potassium ions by 103 times, by magnesium by 278 times, calcium by 25 times.

CONCLUSIONS.

The most important indices of the solid product of low-temperature pyrolysis of poultry manure with litter are determined. It should be noted that the pyrolysis product contains partially non-pyrolyzed components. It is necessary to obtain the product at a higher pyrolysis temperature (degrees per 100-200).

Nevertheless, according to the results of the research, this sample of poultry manure does not meet the requirements of BAU for use as a sorbent, however, it has all the necessary qualities for use as a fertilizer.

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