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LIGNIN SLUDGE APPLICATION FOR FOREST LAND RECLAMATION: FEASIBILITY ASSESSMENT

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The article analyses waste generation of pulp and paper industry in North-Western Russia. The environmental impact of waste storage facilities of the pulp and paper mill was assessed, the need for utilization of lignin sludge was justified. In North-Western Russia, 1.21 million hectares of disturbed areas are in need for reclamation; they are abandoned quarries and lands alienated for pipeline and road construction. The suitability of lignin sludge for preparation of artificial fertile soils for reclamation purposes is estimated. For this purpose, experiments were carried out to create an artificial mixture with different ratios of lignin sludge and soil, to detect the maldevelopment of several plant species grown on various compositions of lignin sludge and soils. It was revealed that lignin sludge as an organic additive to soils is not toxic to vegetation and living organisms, allowing improving fertility of artificial soils.

Key words**:** pulp and paper industry; industrial waste; lignin sludge; waste disposal; disturbed lands; reclamation

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Introduction. The pulp and paper industry is one of the most significant in the Russian Federation, producing about 2 % of the national industrial output. In Russia, there are 270 enterprises of pulp and paper industry, including 20 major plants for cellulose processing with high production capacity (over 100 thousand tons per year), giving 80 % of production in the pulp and paper industry of the Russian Federation [1, 7].

The technological process of cellulose production and processing has hardly changed in Russia since 1950-1970-s. The machines used for cellulose processing are low-productive, with physical wear of more than 80 % and in dire need of replacement or modernisation. The conversion extent of raw materials is 2-3 times lower as compared with developed Western countries [1, 10, 11, 14].

The pulp and paper industry is characterised by high material consumption (it takes an average of 5-6 m^3 of wood to obtain 1 ton of pulp) and water capacity (an average of 350 m^3 of water per 1 ton of pulp), which predetermines the formation of a significant amount of waste. Thus, the manufacture of 1 ton of the end product is fraught with the generation of about 50-80 kg of sewage sludge at biological treatment plants.

Problem statement. The largest volume of non-recyclable waste is generated during wastewater treatment of the pulp and paper industry, resulting in a sewage sludge (lignin sludge), which is stored after removal from the biological treatment plant in specially designated areas withdrawn from economic use. Lignin sludge is a grey mass consisting mainly of excess activated sludge with various inclusions (lignin substances, alumina, polyacrylamide, cellulose fibre, etc.), the number and presence of which differ depending on the cellulose obtaining process. It is common practice to assign the fourth class of danger to lignin sludge, – low-hazard substances with low harmful effects. Despite the low toxicity of the stored waste, sludge tanks have a negative environmental impact.

Sludge tanks impact the atmospheric air with such compounds as sulphur, dioxide, hydrogen sulphide, ammonia, emitted from the decomposing organic part of the waste from biological treatment plants.

The accumulated precipitation (snow and rain), liquefies lignin sludge in the storage, which is particularly wet waste (~75-90 %), and impact underground and surface water; due to this fact, excess water should be removed. Water is removed by pumping and discharge, in some cases without treatment, to the nearest water bodies. The high content of organic substances contained in the sludge waters increases the trophicity of a reservoir, leading to its overgrowing and waterlogging. Apart from that, without proper sludge insulation, toxic substances seepage to the groundwater.

Under the influence of sludge storage on the soil of the surrounding areas, high concentrations of heavy metals (copper, zinc, lead, cadmium, etc.) are found. In addition to the environmental impact, sludge storages become the reason for the alienation of large areas of economic use. This requires studies on the utilization and recuperation of sewage sludge from the pulp and paper industry.

Disposal of such industrial sewage sludge as lignin one reduces the negative burden on the environment and payment for the negative impact of waste storage. This also makes possible to obtain commercial products to be used in industrial or non-industrial areas [12, 13].

Internationally, there are no effective methods of lignin sludge storage reclamation and rational industrial options for waste water disposal. This can be explained by the lack of information about the physical and chemical properties of waste water sludge of pulp and paper industry after its biological treatment due to the complex dispersed composition of both lignin sludge and lignin itself. Without a sufficient understanding of the lignin sludge composition, it is impossible to predict its behaviour in the course of physical, chemical and biological processes of its interaction with the environment. The choice of the method of lignin sludge utilisation is complicated by the high moisture content and hydrophilic nature of the sludge, which makes the processing complex and consuming time and energy.

To date, the methods for utilising lignin sludge are developed mainly in the direction of colloidal sludge incineration, although it is not environmentally effective for a number of reasons:

• incineration only reduces the amount of sludge but does not completely remove it, and the ash obtained from the combustion is delivered to the same storage areas that continue to adversely affect the environment;

• a number of pollutants are released with burning; the load on the air pool increases; the cost of disposal increases when buying and installing highly efficient gas cleaning systems [2, 6, 7].

The possibilities of lignin sludge freezing and consequent utilisation as additives in building materials were considered. Research in the field of creation of vermiculture and vermicompost was carried out. However, the studies had no industrial application and further development. In this regard, the problem of utilisation and recuperation of colloidal sludge generated from biological waste water treatment for the pulp and paper industry is still relevant and requires further research [3, 4, 8].

The issue of development and implementation of an environmentally efficient and economically feasible method of waste disposal for the industry in the North-Western Russia, where 6 of the 10 largest pulp and paper mills in Russia are located, is urgent. Sludge collectors of pulp and paper mill in the North-Western Federal District were chosen as a research object. Man-made dumps, represented by storage cards or sludge storage, occupy up to 30 % of the industrial area of the enterprise, that measures up to hundreds of hectares.

Another difficult environmental problem of North-Western Russia is the presence of disturbed areas represented by mined quarries and lands alienated for pipelines and road construction, with a total area of 121 thousand hectares.

Thus, the purpose of the research is waste utilisation for the pulp and paper industry by creating an effective mixture based on lignin sludge for reclaiming the disturbed lands.

Methodology. To achieve the goal, the following tasks were set:

• Determination of the average composition of lignin sludge stored in the sludge collector.

• Check of lignin sludge for toxicity, the presence of sufficient nutrients necessary for the plant development and growth and the possibility of using lignin sludge as an organic additive to create potentially fertile soils.

• Selection of optimal mixture of lignin sludge with loams used in land reclamation for stable survival and growth of plants.

To assess the average composition of the waste, a combined soil sample was prepared, which included 25 ordinary samples taken in the sludge collector diagonally with a sampler immersed to the full depth of specimen taking. Ordinary samples characterised the complete cross-section of the waste disposal facility. The taken samples were combined into a joint one after individual preparation to a certain stage of reduction (quartering) and then combined in the required proportions. Simultaneously with waste sampling, a brief description of the sampling point location, as well as the extracted material (moisture, colour, particle size distribution, texture, consistency, neoformations and inclusions) was performed.

The selected lignin sludge samples are a mixture of raw sediments and excessive activated sludge in a ratio of ~1:4. Dehydrated waste is represented by curdy crumbs of grey-brown colour, and contains organic matter, phytogenic fibre (lignin), with a pH level of ~ 6.

When determining the suitability of sludge for the creation of fertile compositions used for reclamation of disturbed lands, the following indicators were determined: moisture content, ash content, concentrations of heavy metals, and organogenic elements – nitrogen, phosphorus, carbon, hydrogen, calcium – necessary for plants, especially in acidic soils. The studies were conducted to compare the results with the existing indicators regulated in normative documents.

The moisture content of lignin sludge was determined using a rapid moisture analyser – the MX-50 moisture meter. Studies have shown that the moisture content of the combined sample of lignin sludge is 70-75 %, which is comparable to the humidity of medium-loamy and light-loamy soils.

To determine the mass fraction of mineral fraction, the ash content of the sludge was determined by calcining samples of lignin sludge in a muffle furnace at a temperature of 750 °C [5]. Studies have shown that the ash content of lignin sludge is 4 % in terms of the air-dry sample. Thus, the organic component in the waste of the pulp-and-paper mill (PPM) has an extremely high content of 96 %, exceeding the content of organic substances in most types of peat (80-85 %) and sapropel (about 90 %), due to the presence of lignin fibre in the sediment.

The contents of carbon, hydrogen and nitrogen were determined in the air-dry state of lignin sludge samples using the LECO CHN628 analyser. Measurement result, %: carbon 47.057, hydrogen 5.712, nitrogen 0.310 (sample 1); carbon 47.359, hydrogen 5.839, nitrogen 0.410 (sample 2).

Qualitative chemical analysis of lignin sludge was carried out using the ICPE 9000 atomic emission spectrometer to determine the presence of heavy metals. The lignin sludge ash sample was dissolved in a solution of nitric acid and hydrochloric acid, then evaporated at a temperature of 90 °C until the salts were completely dissolved. The results of studies of lignin sludge samples showed the presence of the following elements: Cu, Zn, traces of Mn, Fe, Al, B, Mg, Na.

Quantitative analysis of lignin sludge was carried out using the Shimadzu AA 7000 atomic absorption spectrometer. Samples of solutions prepared earlier for qualitative analysis were analysed. Measurements showed that the average zinc content of 430 mg/kg, copper – 210 mg/kg, calcium – 7.87 %.

The phosphorus content was determined using the DR 5000 spectrophotometer. Prior to the formation of orthophosphates, the sample was pre-dissolved by adding ascorbic acid and acid mo-

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lybdenum solution, and analysed. The analysis showed that the average phosphorus content in the lignin sludge sample of 0.155 % of the total sludge mass.

Discussion. When evaluating lignin sludge suitability to create a fertile soil mixture, the following regulatory instruments were considered: the GOST R 17.4.3.07-2001 «Nature protection. Soils. Requirements for sewage sludge use for fertilisation» and the GOST R 54651-2011 «Organic fertilisers on the basis of sewage sludge. Specifications». The results of the comparison of normative levels with those obtained for lignin sludge are given in Table 1.

Table 1

Assessment of lignin sludge suitability for amending a fertile soil mixture

Indicator	GOST R 54651-2011		GOST R 17.4.3.07-2001		Lignin sludge
	I*	II**	I	II	
Mass fraction of potentially toxic elements, mg/kg of dry matter, not more than:					
Lead	130	250	250	500	Not detected
Cadmium	2	15	15	30	Not detected
Zinc	220	1750	1750	3500	430
Copper	132	750	750	1500	210
Nickel	80	200	200	400	Not detected
Chromium	90	500	500	1000	Not detected
Mercury	2.1	7.5	7.5	15.0	Not detected
Arsenic	2	10	10	20	Not detected
Mass fraction of organic matter per dry sample, %, not less	70		20		96
Activity index of hydrogen ions of salt suspension, pH units	6.0-8.0		5.5-8.5		6.0
Mass fraction of nutrients, %, not less:					
Total nitrogen	0.60		0.60		0.36
Total phosphorus	0.70		1.50		0.155
Total potassium	0.1		–		–

* Fertilizers of the group I on the basis of sewage sludge used for cultivation of technical, fodder, grain and green manure crops.
** Sewage-sludge-based fertilisers of the group II used in the planting of forest crops along roads, in nurseries of forest and ornamental crops, floriculture, cultivation of depleted soils, reclamation of disturbed lands, road slopes and landfills.

The results of the comparative analysis (Table 1) showed the possibility of using lignin sludge for forest reclamation due to the practical absence of potentially toxic elements. Studies have shown that in the waste, despite the high content of organic carbon, there is a significant deficit of nitrogen (two times lower) and phosphorus (10 times lower) as compared to the standards for fertilisers.

To develop the optimal composition of fertile mixtures with lignin sludge, experiments were conducted to create artificial soils with different ratios of lignin sludge and soil, and to study the plant growth on different compositions of lignin sludge and soil.

For the experiment, 5 boxes of 130×270×120 mm size were selected, in which soil and lignin sludge mixtures were prepared in different weight proportions. The selected soil was a light loam with a neutral pH level, belonging to very poor soil, having the following content of mineral nutrients: 50 mg/kg of nitrogen, 150 mg/kg of phosphorus and 250 mg/kg of potassium. This soil was chosen to prove the possibility of using lignin sludge in combination even with poor, low-nutrient soils, without negative impact on the flora of the reclaimed areas. The ratio of the introduced masses of soil and lignin sludge for several studied models is presented in Table 2.

All five models of artificial soil were in the same conditions in a well-ventilated area for 10 weeks at a constant temperature of 25 °C and a relative humidity of 70 %. Twice a week, 50 ml of

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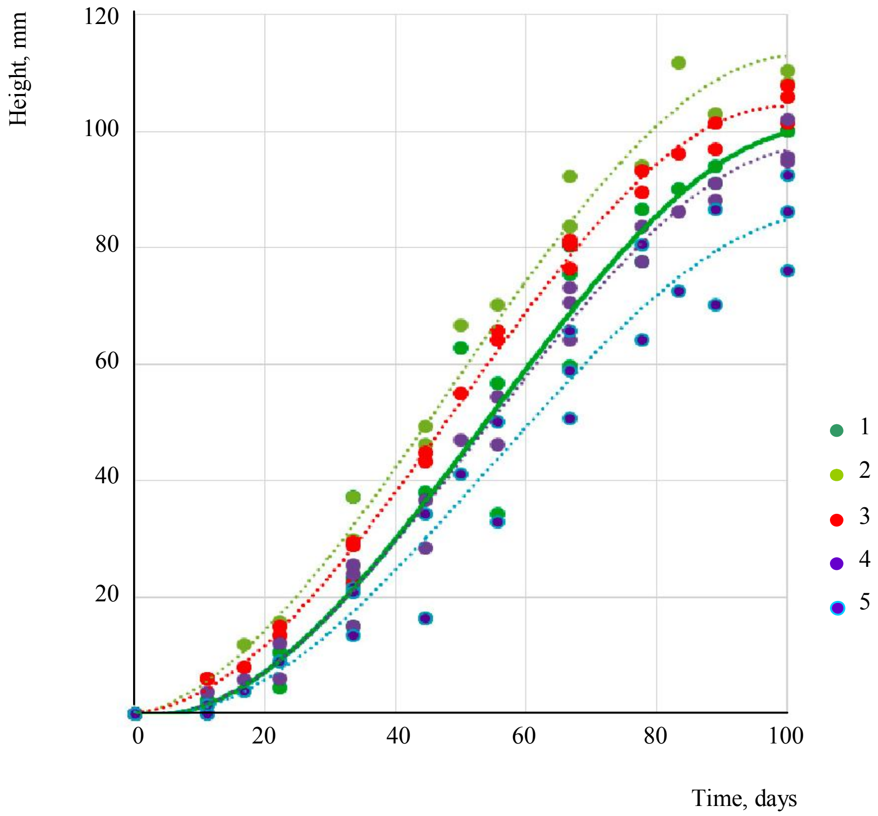
Table 2

The ratio of used masses of soil and lignin sludge

Sample	Sludge, %	Sludge weight, g	Soil, %	Sludge weight, g
Test sample	0	0	100	1200
1	15	180	85	1020
2	35	420	65	780
3	55	660	45	540
4	75	900	25	300



Combined graph of plant growth rate and time

1 – control sample; 2 – mixture with 15 % of lignin sludge; 3 – with 30 %; 4 – with 50 %; 5 – with 75 %

water was added to each box (based on the normal requirements for the selected herbaceous plants). The indoor lights for growing plants were turned on at a height of 0.5 m daily from 9 am to 5 pm.

Seeds of wild herbs of mixed coniferous-broad-leafed forest were added to the artificial soils in accordance with the sowing norms: red clover (*Trifolium pratense*) – 10 g/box; herb mixture – 5 g/box: meadow fescue (*Festuca pratensis*) – 34 %, Timothy-grass (*Phleum pratense*) – 30 %, perennial ryegrass (*Lolium perenne*) – 28 %, festulolium (*Festulolium*) – 8 % and bentgrass (*Agrostis*) – 6 g/box.

Regular measurements of plant growth and the presence of external indicators of oppression were carried out. During the experiment, no external signs of developmental disorders, chlorosis and necrosis were observed in plants. At the end of the 10th week, after reaching the maximum growth of all plant species, the experiment was stopped, all types of herbs were cut and weighed to establish the total aerial part of the biomass. The results of the research allowed to determine the aerial biomass of grasses on 1 m^2 of the territory for different types of soil mixtures: control sam-

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ple – 500 g; first type (15 % of lignin sludge) – 635 g; second type (30 %) – 624 g; third type (50 %) – 621 g; fourth type (75 %) – 265 g.

The lowest grass mass was grown in the fourth box, containing 75 % of lignin sludge, due to the high water-holding ability of the sludge, and consequently, the overwetting of the artificial soil. The remaining boxes showed an increase in biomass compared to the control sample by 25 %, which indicates a favourable effect of lignin sludge on plant development.

During the experiment, the average plant growth was measured weekly to confirm the absence of plant development disorders. Calculations were carried out on the basis of logistic dependence of plant growth dynamics in time:

$$\frac{dl}{dt} = \mu l\left(1 - \frac{l}{l_{\max}}\right),$$

where t is for the time; l is for the current plant height; $l_{\max}$ is for the maximum height; and μ – is for the constant (specific growth rate).

After the processing, a combined data matrix on the growth rate of plants on all types of artificial soils was drawn. On the basis of the data obtained, the graphs of the growth rate of plants of each type with the values of sample reliability are constructed (Figure).

The calculation of the average specific rate of plant growth by the least squares method showed that deviations from the control sample exceeding 20 % are not observed in any artificial soil, respectively, there is no toxic effect of lignin sludge. Results of determination of growth factors (specific growth rate): control sample – 0.787; artificial mixture with 15 % of lignin sludge – 0.747; with 30 % – 0.798; with 50 % – 0.846; with 75 % – 0.929.

Conclusion. The conducted research allowed to draw the following conclusions:

1. The most promising method of waste disposal in the pulp and paper industry is the creation of artificial soils based on the addition of lignin sludge in the share of 15-30 %, which can be used as an organic amendment.

2. Lignin sludge as an organic additive to soils is not toxic to vegetation and allows to improve the fertility of artificial soils.

3. Artificial soils created on the basis of a mixture of light loam and 15-30 % of lignin sludge, contribute to an increase in the growth rate of vegetation cover by 15 % and aerial biomass by 25 %.

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