Original article



# On the possibility of utilizing sodium lignosulfonate as a nano-organic foundation for creating soil-like bodies in the purposes of technogenic-degraded land rehabilitation

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ABSTRACT: Introduction. Currently a significant number of quarry restoration strategies have been developed, based on different aspects of soil impact: specifically, mixing the topsoil with the empty rock of exhausted quarries; introducing organic waste; applying mulching and polymer structure formers; using the adapted plants. In this study we attempt to combine the positive aspects of the previously mentioned methods. Therefore, the aim of our research is to create artificial soil-like structures with specified agroecological properties. We anticipate further use of the obtained mixture as a layer between the guarry waste material and fertile soil, which is to be applied to the reclaimed surface and followed by the planting of local plant species. Materials and methods. Studies on the possibility of reclamation of mine tailings were conducted under conditions of model experiment with sodium lignosulfonate (SL), a waste organic material from the pulp and paper industry, as the organic base for the soil-like body. Fine fraction soil (FS) sampled from the mine tailings was mixed with SL in ratios of 1/0.5, 1/1, and 1/2; to accelerate the decomposition of organic matter depending on the experimental scheme, strains of bacteria Acinetobacter calcoaceticus and Pseudomonas kunmingensis were added. The obtained mixtures have been composting for three months at a room temperature, with regular mixing and maintaining moisture levels. The phytotoxicity of the obtained mixtures was assessed by germinating seeds of a short duration radish variety called "18 days". Results and discussion. The application of sodium lignosulfonate (SL) into the fine fraction soil (FS) significantly increased the organic matter content and decreased the acidity of the medium. The fertilizing with nitrogen in the SL experimental variants has led to a significant increase in the content of alkali-hydrolysable nitrogen compared to the variants in the absence of N and the presence of SL. Conclusion. The research results showed that the application of sodium lignosulfonate (SL) to the fine fraction soil (FS) contributed to a decrease in acidity, an increase in organic matter and alkali-hydrolysable nitrogen content in the mixture, as well as a reduction in substrate toxicity.

KEY WORDS: sodium lignosulfonate; quarry reclamation; nano-fertilizer; microorganisms.

**ACRONYMS LIST:** SL – sodium lignosulfonate; FS – fine fraction soil of quarry waste; MO – microorganisms; OM – organic matter; AHN – alkali-hydrolysable nitrogen; N – mineral nitrogen fertilizer.

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### INTRODUCTION

Recent studies based on satellite space monitoring show that the loss of the planet's topsoil amount to 16 million hectares annually [1]. Meanwhile, the population of the planet is growing, and the impact of climate change on natural ecosystems is worsening the issue [2, 3]. In such circumstances, the land shortage needs to be prevented not only through methods of controlled agriculture and soil degradation prevention, but also by actively restoring lost fertile territories. The reclamation of abandoned quarries can provide new types of land use



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and mitigate the consequences of soil erosion [4, 5], while the development of secondary forests on degraded areas is of interest due to their potential in carbon sequestration [6]. However, many of the abandoned quarries are not subjected to targeted reclamation, and the self-restoration of disrupted ecosystems can take many years or even decades [7, 8].

In cases of reclamation, the most effective restoration strategy is the application of a soil cover by returning the removed top layer and planting vegetation on the reclaimed areas [9]. In arid and semi-arid regions, the use of such a method is limited by climatic factors such as high evaporation rates and low precipitation amounts. Areas with adverse conditions often face the problem of insufficient suitable soil for creating a new fertile layer [10].

Anthropogenic pressure while the extraction of minerals also creates a negative impact on the biological activity of the region's soils [11]. As a result, even with timely reclamation, the newly created soils do not possess the necessary physical, chemical, and biological characteristics to support a sustainable ecosystem. Soil characteristics directly affect erosion development, plant root development, density and coverage, all of which determine the development of natural vegetation and are key factors in assessing ecological restoration [9].

Over the past years, numerous quarry restoration strategies have been developed based on various aspects of soil impact. There are methods for improving the agrochemical composition of newly developed soils in rehabilitated areas, for example, through the introduction of organic waste [13, 14]. Landscape methods also exist, which involve reducing erosion and protecting soil from adverse climatic conditions by decreasing evaporation and increasing infiltration, such as mulching and the use of polymer structure-formers [15, 16]. Multiple strategies for restoration have been described that are not based on the addition of ameliorants to soils, but rather on creating more resilient ecosystems under conditions that already exist or have minimal impact on soils, for example, the use of plant species adapted to nutrient and water limitations for reclamation. Vegetation with morphological and physiological adaptations to survive and grow in harsh conditions of arid and semi-arid regions is more successful in resisting negative environmental factors [17, 18]. There are also studies [19, 20] that examine the increase in the amount of substrate introduced for reclamation by mixing the topsoil layer with waste rock from exhausted quarries. The authors of the mentioned studies concluded that as a result, the organic matter content increased in the overall mixture, probably due to the improvement of the hydrological function and biomass production, as well as the activity of microorganism dehydrogenases. The improvements spread deeper into the soil profile, thus contributing to the soil function restoration.

Any of the above strategies contributes to the processes of reclamation of disturbed areas, but has its own drawbacks. In the case of adding ameliorants, there are limitations in the ecological requirements for the content of heavy metals, nutrients, acidity of the environment, or resistance to water and wind erosion, even without considering economic factors. In addition, the effective use of ameliorants implies not only improving soil properties but also providing mineral nutrients in accordance with the needs of vegetation. The use of stable plant species for land reclamation should not create competition for the local existing flora, as it negatively affects the region's ecosystems as a whole [21, 22]. The method of mixing soil and quarry rock is limited as the rock is to have a specific structure and should not contain substances that hinder the development of vegetation. For many nonferrous and heavy metals extracting quarries, this condition is not met, as they almost always contain significant amounts of harmful elements for living organisms. In the current research, we attempted to combine the positive aspects of the methods mentioned earlier. To achieve that, we assessed the addition of sodium lignosulfonate (SL) to the substrate sampled from quarry dumps. We propose to further use the resulting mixture as a layer between the quarry dump material and fertile soil, which will be applied to the reclaimed surface and followed by the planting of local plant species.

Widely known, that it is economically efficient utilizing production organic waste as ameliorants. This allows reducing pollution of the environment when accumulating the sludge and using it beneficially in agriculture [13, 23, 24]. In this regard, SL is one of the promising substances. In the process of the chemical processing of wood in cellulose-paper and hydrolysis plants the most difficult-to-utilize part of cellulose – lignin, becomes waste and is usually sent to the storage facilities, where it can be stored for decades due to the limited waste recycling and high resistance to decomposition. The high acidity of such lignin has a negative impact on the environment, acidifying the soil and water, polluting the air basin, and being a dangerous source of ignition [25, 26]. On the other hand, lignin is a natural resource that provides renewable aromatic compounds and is structurally similar to the non-hydrolysable part of humic acid. As a soil additive, it can serve as a source of organic carbon, improving soil nitrogen balance as 1g of carbon helps fix 15–20 mg to 40 mg of atmospheric nitrogen [27, 28], and as a basis for the accumulation and gradual release of mineral components. Lignin is a major component of lignosulfonate. In terms of its impact on the environment, LS has proven sorption ability towards heavy metals, including as a substance used in the treatment of industrial wastewater [29, 38], meaning it will suppress the toxic effects of quarry material. The anti-erosion resistance of SL, highlighted in its use in road construction [31, 38],

will also add a positive effect. Thus, SL can serve both as a substance improving the agrochemical composition of the soil, and as a structural former, and as a component of quarry material, reducing toxicity and allowing for a reduction in the amount of soil used for forming the top layer.

Numerous compositions based on SL have been developed to be used as alternatives to conventional fertilizers in agriculture [25, 33]. Researchers generally agree that the application of SL is more effective when: a) used in combination with mineral components as a source of nutrients for plants [34], and b) after pre-composting to reduce acidity and increase its bioavailability, usually with the involvement of microorganisms that facilitate the decomposition of SL [35, 38, 37, 38]. In the first case, SL is used as a matrix to retain mineral components, while in the second case, it serves as a source of humic substances.

Based on all the aforementioned facts, a model experiment was conducted in laboratory conditions to investigate the possibility of creating soil-like bodies through composting a mixture of sodium lignosulfonate (SL) and fine fraction of quarry waste (FS) with microorganisms additives (MO) and nitrogen fertilizer (N).

#### 2. MATERIALS

**2.1 Fine fraction soil of quarry waste (FS).** We used for the experiment material from the waste dump of the Kulurtay mine quarry, located in the Baymak district in the southeast of the Republic of Bashkortostan. The deposit was used for the extraction of oxidized gold-bearing ores, copper, zinc, and alluvial gold. The waste rock was stored by forming waste dumps. Currently, mining operations have been completed, the quarry is flooded, and the area has a heavily disturbed relief, with the natural soil cover removed. No reclamation has been carried out after mining cessation. Self-overgrowing has been for at least 30 years (since 1985), and there are visible patches of secondary soil cover formation on the quarry waste dumps, presumably partially alluvial and partially formed

in situ. The vegetation is represented by young birch and pine bushes, with no grass cover.

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The material of the quarry waste is dry, white, powdery, with inclusions of yellow and dark orange, represented by grus and gravel. According to literature sources [40], its composition is similar to that of extracted ores and contains elements such as copper, zinc, gold, and silver. The overburden consists of basalts-andesites-basaltsandesite-dacite-riolite subformation of andesite-basalt formation [41]. The content of organic carbon is 0.5%, alkali-hydrolyzable nitrogen is 42 mg/kg of fine sand, and the medium's reaction is strongly acidic (pH H<sub>2</sub>O – 2.9).

The area is characterized by dryness and insufficient moisture supply: the sunshine duration is 1950–2000 hours per year; the average annual air temperature is  $1.5-2^{\circ}$ C; the average air temperature in July is  $17.5-18^{\circ}$ C; the amount of precipitation per year is 350-400 mm; the amount of precipitation during the warm period is 250-300 mm; the average number of days with atmospheric drought is 40-45 days per year; the average wind speed is 3.5-4 m/s. The area is distinguished by a high anthropogenic pressure on the natural environment, caused by both mining industry and intensive agriculture [42].

For the model experiment, samples weighing at least 1 kg were collected from multiple points within the inner part of the external quarry slope. The samples were mixed, cleared of large fragments, stones, and plant residue, and sifted through a sieve with a diameter of 1 mm. From the obtained quantity, a portion of approximately 50 g was separated by quartering method for agrochemical analysis of the original substrate. The remaining portion was thoroughly mixed and used in the experiment.

**2.2. Sodium lignosulfonate (SL).** We used for the experiment waste from a pulp and paper mill, available for purchasing. The liquid form of SL with the technical characteristics presented in the Table 1 was used.

**2.3. Mineral Fertilizer (N).** In the experiment we used a preparation with a trade mark "Mixed Mineral Fertilizer Ammonium Nitrate with a Complex of minor nutrient elements, N - 33%" produced by LLC "TPK NOV-AGRO". The content of nutrients by mass frac-

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Technical characteristics of sodium lignosulfonate	
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Appearance	Viscous liquid of dark color
Mass fraction of dry matter, %, no less than	50
Ash content to the mass of dry matter, %	27
Hydrogen ion concentration, pH, no less than	4.5
Tensile strength of dried samples, MPa	0.6
Conditional viscosity, sec, no less than	80
Mass fraction of reducing substances to the mass of dry matter, %	15
Density, kg/m <sup>3</sup> , no less than	1280





tion: nitrogen (N) - 33%, boron (B) - 0.03%, copper (Cu) - 0.15%, iron (Fe) - 0.09%, manganese (Mn) - 0.16%, molybdenum (Mo) - 0.002%, zinc (Zn) - 0.04%. The application rate depends on the culture and ranges from  $15-20 \text{ g/m}^2$ .

**2.4. Microorganisms (MO).** Strains Acinetobacter calcoaceticus UOM 22 and Pseudomonas kunmingensis CA 3, with proven ability to degrade hydrocarbons [44, 45, 45] were used. Cultures were grown up in the laboratory of biotechnology at the Ufa Institute of Biology, Ufa Federal Research Center of the Russian Academy of Sciences. Strains were separately cultivated in liquid medium King B [46], and then mixed in equal proportions. The concentration of microorganisms in the solution was approximately 109 CFU/mL. The recommended dosage for application was 1 mL of the microorganism solution per 300 g of substrate.

**2.5. Radish.** The phytotoxicity of the obtained mixtures was evaluated by germinating seeds of the fast-growing radish variety called "18 days" [47].

## **3. METHODS**

The experiment was conducted in vegetative containers according to the scheme presented in the Table 2.

Pre-purified fine fraction soil of quarry waste was sieved for more effective interaction with the introduced additives. In the experiment, we used smaller than 1 mm fraction. The amount of introduced SL was calculated on the given weight ratio. Rate of complex fertilizer application N was 1 g per container. Microorganisms were added at a quantity of 1 ml per 300 g of substrate. After all components were added (except microorganisms, which were added by mixing them in the water for irrigation), the mixtures were thoroughly mixed, then 100 ml of distilled water was added to each mixture and mixed one more time. The obtained samples were left for composting under laboratory conditions at a temperature of  $25-26^{\circ}$ C, natural lighting, and ventilation. The vessels were moistened as needed, and the number of irrigations and the volume of water were recorded. Every two weeks, after being preliminarily watered and thoroughly mixed, a portion of 20-25 g of the samples was taken for analysis and placed into a freezer to deactivate the life activities of microorganisms.

Sampling for investigation by the composting time were taken at a  $3^{rd}$  day (1st period), a  $7^{th}$  day ( $2^{nd}$  period), a  $13^{th}$  day ( $3^{rd}$  period), a  $27^{th}$  day ( $4^{th}$  period), a  $41^{st}$  ( $5^{th}$  period),  $56^{th}$  ( $6^{th}$  period), and an  $82^{nd}$  ( $7^{th}$  period) day (completion of composting). After the completion of composting, the soil-like mixture was dried to an air-dry state and re-analyzed at a  $250^{th}$  day ( $8^{th}$  period) from the launch of the model experiment.

In the selected samples, the content of organic matter (OM) was determined with the Turin method with completion by Orlov and Grindel method, the alkalihydrolysable nitrogen (AHN) was determined with the Kornfield method, and the pH of the aqueous suspension was determined potentiometrically [39].

Composted mixtures were tested for phytotoxicity with fast-growing radish seeds. A ground and sieved through a 1 mm sieve sample (1 g) was mixed with 10 ml distilled water, stirred. A filter paper was impregnated with the resulting solution. Ten seeds were placed on the surface of the moist

# Table 2 Scheme of the model experiment

Experimental entions	Composition of the mixture			
(proportions)	Fine fraction soil of quarry waste, g	Sodium lignosulfonate, g	Nitrogen fertilizer, g	Culture bacteria, ml
1. Control (FS)	300	—	—	—
2. FS/SL (1/0.5)	300	150	_	_
3. FS/SL (1/1)	300	300	_	_
4. FS/SL (1/2)	300	600	_	_
5. FS/SL (1/0.5) + N	300	150	1	_
6. FS/SL (1/0.5) + N + MO	300	150	1	1.5
7. FS/SL $(1/1) + N$	300	300	1	_
8. $FS/SL(1/1) + N + MO$	300	300	1	2
9. FS/SL (1/2) + N	300	600	1	—
10. FS/SL (1/2) + N + MO	300	600	1	3
11. FS + MO	300	_	_	1
12. FS + N + MO	300	_	1	1

paper. Control tests were also conducted with filter paper impregnated with distilled water and water extract from FS. Phytotoxicity was evaluated based on the number of germinated seeds and the dry mass of seeds and seedlings in 48 hours. The test was repeated three times for each sample. The obtained data were processed statistically.

## 4. RESEARCH RESULTS

In three days following the beginning of composting (first period), the initial series of samples was collected for examination. The introduction of SL to FS considerably enhanced the content of organic matter and decreased the acidity of the medium. The organic matter content displayed a proportional increase in relation to the growth of SL. Sodium lignosulfonate concentration did not significantly impact the acidity of the fine fraction soil and the content of alkali-hydrolysable nitrogen (Fig. 1, experimental variants 2–4).

It is known that the decomposition of SL occurs slowly, and the availability of organic matter for plant nutrition from it is low [25, 33]. Microorganisms and/or nitrogen fertilizers have been used to intensify the process of organic matter decomposition from SL [34, 35, 36, 37, 38]. Additionally, the application of nitrogen-containing substances contributed to the increase of the extremely low nitrogen level in the substrate (Figure 1b, experimental conditions 5–10, 12).

The application of nitrogen fertilizer on the variants with sodium lignosulfonate compared to variants containing only lignosulfonate led to a significant increase in the content of AHN – alkali-hydrolysable nitrogen. The amount of organic matter was slightly lower compared to similar samples in the absence of N, indicating the beginning of its decomposition process (Fig. 1a). The smallest difference in organic matter content in experimental variants with only lignosulfonate and lignosulfonate + N was observed in the variant 5 (FS /SL (1/0.5) + N). This variant also showed the least increase in the amount of alkali-hydrolysable nitrogen, which does not correspond to the trend of nitrogen fertilizer distribution in the substrate mass (Fig. 1b).

Variant 5 (FS/SL (1/0.5) + N) by mass contains 450 grams of substance, variant 7 (FS/SL (1/1) + N) – 600 grams, and variant 9 (FS/SL (1/2) + N) – 900 grams. However, with the same amount of nitrogen fertilizer applied to these variants, the smallest increase in its content was observed in variant 5 (FS/SL (1/0.5) + N). This result is likely due to an excessive amount of N on the substrate

Fig. 1. Agrochemical properties of SL based mixtures in different periods: the  $1^{st}$  period - 3 days of composting; the  $7^{th}$  period - 82 days of composting; the  $8^{th}$  period - 6 months of after finishing composting





■ 7th period ■ 8th period

■1st period



mass, which led to denitrification of nitrogen fertilizer and reduced its beneficial effect. The reaction of the environment in variants with SL and N is similar to variants with SL in the absence of N – the acidity decreased from 2.8 to 4.1-4.4 pH units in all samples (Fig. 1c).

The reaction of microorganisms to sodium lignosulfonate was evaluated with additional variants 11 and 12, with the presence of microorganisms in fine fraction soil and the absence of SL (variant 11); and presence both microorganisms and N (variant 12). According to the analysis results (Fig. 1), it can be seen that the addition of microorganisms to the fine fraction soil without the addition of any other substances does not have a significant effect on its agrochemical properties. The addition of microorganisms in combination with nitrogen fertilizer leads to a significant increase in soil humic acids content and slightly increases the acidity of the medium (up to pH 3 H<sub>2</sub>O). At the same time, the concentration of N in the substrate was highest among all samples (1 g of fertilizer per 300 g of substrate), but no loss of nitrogen effect, as discussed in variant 5 (1 g of fertilizer per 450 g of substrate), was observed.

The amount of sodium lignosulfonate added influenced the dynamics of changes in the content of organic matter and alkali-hydrolysable nitrogen in the mixture of with SL, N, and microorganisms (MO). For the variants FS/SL in the ratio of 1/0.5 and 1/1, the content of organic matter was higher compared to the variants containing nitrogen (by 0.3% and 4.8%, respectively), but lower than in the variants with only sodium lignosulfonate (by 2.3% and 1.8%, respectively). Alkali-hydrolysable nitrogen in the presence of microorganisms is higher in the 1/0.5 ratio variant compared to only N (210 mg/kg in the variant FS/ SL + N versus 406 mg/kg in the variant FS/SL + N +MO), but becomes lower in the 1/1 ratio variant compared to the corresponding N-only sample (322 mg/kg in the variant FS/SL + N versus 308 mg/kg in the variant FS/SL + N + MO). Variants with the FS/SL (1/2) ratio demonstrate a decrease in both organic matter content (62.7% for the FS/SL variant, 54.4% for FS/SL + N, and 53.8% for FS/SL + N + MO) and alkali-hydrolysable nitrogen (308 mg/kg for FS/SL + N versus 140 mg/kg for FS/SL + N + MO) (Fig. 1).

The assessment of the agrochemical condition of soil-like bodies according to the experimental variants, conducted both at the end of the experiment (the 7<sup>th</sup> period) and for the second time after drying (the 8<sup>th</sup> period), showed that the medium reaction of all samples with additives became less acidic over time. In all of the variants, except for the control (variant 1 - fine fraction soil), the acidity values were decreasing (although insignificantly, but consistently for all samples) even after composting, indicating the influence of the introduced components and the continuation of the substrate neutralization reaction (Fig. 1c).

The dynamics of organic matter change was similar in all samples, except for the variations with the FS/SL ratio of 1/0.5. In other cases, samples with additives were characterized by an increase in organic matter content after 82 days of composting (7th period) from 3.24% to 38.27% (maximum value, variant 10 - FS/SL(1/2) + N + MO), followed by a decrease in the level of organic matter content below the initial level by 2.62% (variant 10 - FS/SL(1/2) + N + MO to 28.58% (variant 4 - FS/SL (1/2)). This reaction is likely due to the growth of microbial mass in the nutrient medium of SL, with a tendency to increase the amount of organic matter with increasing concentration of sodium lignosulfonate and the addition of microorganisms. While substrate was drying (8th period), a decrease in organic matter content was observed [48]. In the variants with a ratio of components FS/SL (1/0.5), the dynamics of changes in OM depending on the additives was less pronounced, while the amount of OM after composting and drying of samples (the 8th period) increased or corresponded to the initial content of OM. In the variants 11 (FS+ MO) and 12 (FS + N + MO), no significant changes were observed. It should be noted that in variant 12 (FS + N + MO), the content of organic matter increased to 1% at the 7th period of sampling and then decreased to 0.3% after 6 months of composting (8<sup>th</sup> period), which may indicate the prolonged action of microorganisms and their ability to develop in pure fine fraction soil in the presence of nitrogen-containing fertilizers (Fig. 1a).

The change in the content of alkali-hydrolysable nitrogen unidirectionally followed the dynamics of organic matter in the samples. In the overall scheme, samples with the FS/SL ratio of 1/0.5, with no significant changes in alkali-hydrolysable nitrogen content over time, were observed (Fig. 1b).

Testing the obtained mixtures for phytotoxicity showed 100% seed germination in all experimental variants. Radish sprouts appeared simultaneously on the second day of germination and reached a height of 3–4 cm by the end of the germination period (Table 3).

The most successful variant of radish cultivation was observed for a mixture with a ratio of FS/SL (1/0.5) in the presence of nitrogen fertilizer and microorganisms (dry biomass growth was 82.35%) (Table 3).

After completing the experiment and evaluating the samples for organic matter content, alkali-hydrolysable nitrogen, and pH  $H_2O$  medium, the obtained data were analyzed with computational methods.

The calculations were performed taking into account the agrochemical analysis data of intermediate samples for all variants based on the following predictors:

1. Initial concentration of introduced additives (SL, N, MO);

2. Number of composting days for all sampling periods: from the  $1^{st}$  to the  $8^{th}$ .



#### Table 3

# Germination rate and dry weight of radish seeds and sprouts

Experimental Variants Phytotoxicity	Share of sprouted seeds, %	Dry weight seeds, g	Dry weight increase, %
1. Control (FS)	100	0.12	21.74
2. FS/SL (1/0.5)	100	0.12	33.33
3. FS/SL (1/1)	100	0.12	50.00
4. FS/SL (1/2)	100	0.13	8.33
5. FS/SL (1/0.5) + N	100	0.12	16.67
6. FS/SL (1/0.5) + N + MO	100	0.09	82.35
7. FS/SL $(1/1) + N$	100	0.14	30.43
8. FS/SL (1/1) + N + MO	100	0.14	14.29
9. FS/SL (1/2) + N	100	0.12	14.81
10. FS/SL (1/2) + N + MO	100	0.12	15.38
11. FS + MO	100	0.12	21.74
12. FS + N + MO	100	0.10	33.33
13. Control (on filter)	100	0.13	36.00

A regression analysis was conducted to identify the relationship between these factors and the content of organic matter, alkali-hydrolysable nitrogen, and pH  $H_2O$  (Table 4, 5).

Upon the analysis, it is possible to assess the presence and direction (direct or inverse) of the relationship between predictors and changing factors, as well as the degree of their influence on each other. The obtained values of regression statistics (Table 4) indicate the following:

1. The proportion of explained variations (coefficient of determination: R-squared) for all three evaluated indicators is above 0.8 (above 0.9 for OM), demonstrating the high quality of the used model;

2. The Adjusted R-squared decreases slightly, confirming the optimal choice of the number of predictors.

# Table 4Regression statistics data

Indicator	OM, %	AHN, mg/kg	рН Н <sub>2</sub> О
Multiple R	0.96	0.91	0.90
R-squared	0.92	0.83	0.82
Adjusted R-squared	0.91	0.82	0.81
Standard error	6	60	0.24
Observations	96	96	96

### Table 5

# Coefficients obtained on the application of the regression analyses to assess the degree of influence of predictors on the changing factors of OM, AHN, and pH H<sub>2</sub>O

Indicator	OM, %	AHN, mg/kg	pH H <sub>2</sub> O
Y-intercept	-0.16	40.61	3.18
Duration, days	-0.0002	-0.0625	0.0011
Application of SL, g/g	81.67	25.36	1.96
Application of N, mg/g	-0.63	116.22	0.09
Application of MO, ml/mg	0.80	2.99	-0.0003

Based on the above, it can be assumed that the influence coefficients provide a fairly accurate representation of the significance of each factor in the linear regression. Analysis of the coefficients numerical values showed that the organic matter content is primarily influenced by the amount of SL applied, the change in AHN quantity occurs with the addition of nitrogen, and the soil acidity depends on the application of SL (Table 5).

The values obtained from the calculations are consistent with experimental data and are logically consistent, which is visually confirmed by convergence plots displaying the relationships between experimental and calculated data for each changing factor (Fig. 2).

#### 5. DISCUSSION

As noted earlier, for all mixtures containing sodium lignosulfonate, there was an increase in the organic matter and a shift of the reaction medium towards the neutral (Fig. 1a and 1c). The addition of mineral nitrogen fertilizer was a key factor in increasing the content of alkali- hydrolysable nitrogen (Fig. 1b). Regression analysis confirmed that the main predictors with the greatest weight in the formula of the linear regression equation and with a positive impact are the concentration of SL in the mixture for the organic matter and pH of the medium, and the concentration of nitrogen for the alkali-hydrolysable nitrogen content (AHN) (Table 5). The remaining predictors influence the changing factors as follows:

- For the content of organic matter without taking into account the factor that has the main significance (SL concentration): additional application of MO has a positive influence, negative influence – application of N and composting period;
- For the AHN content (without N application): SL concentration and application of MO have a positive influence, but the period of composting has a negative influence;
- For pH (without considering SL concentration): N application and composting period have a positive influence, but MO input has a negative influence.

Such conclusions provide a general direction of the influence of additives on the mixture but do not reflect the essence of the processes occurring when the components interact over time. Let's consider the dynamics of the measured factors for a better understanding of the mechanisms of interaction between them and predictors, based on the ratio of fine-grained soil/sodium lignosulfonate in the mixture.

> Fig. 2. Convergence graphs between experimental and calculated data for the OM content (graph a), AHN (graph b) and pH H<sub>2</sub>O (graph c)





5.1. Soil grounds with a ratio of SF/SL - 1/0.5. Addition of SL increased the organic matter (OM) content at the beginning of the experiment (1<sup>st</sup> period) up to 30.7%; for the variant with just SL (Variant 2 - FS/SL), but compared to this variant, the OM content was lower by 2.3% for the mixture with N (Variant 5 - FS/SL + N) and by 2% for the mixture with N+MO (Variant 6 - FS/SK + N + MO (Fig. 1). By the 8<sup>th</sup> period, the OM content decreased by 0.9% for the mixture with SL without additives. However, for the variants 5 and 6 (FS/SL + N and FS/SL + N + MO), there was an increase in OM content relative to the initial values by 1.6% and 4.5%, respectively (Fig. 1a). Probably, the decrease in OM content at the beginning of the experiment may indicate that some of it was consumed for the nutrition of microorganisms, and further increase indicated the growth of the bacterial pool, with the bacterial biomass being higher where additional MO was provided. Thus, when the content of organic matter (OM) in the mixture remained at the same level or slightly increased relative to the initial level, its bioavailability in the soil presumably increased. It should be noted that the OM content in the sample with the only SL decreased by 2.9% after 82 days of composting (7th period) compared to the initial content, but then increased by 2% by the 8th period. Such results can be explained by carbon emission during the composting process and subsequent sequestration from the atmosphere when drying the sample, as well as by the ability of microorganisms (MO) in the FS to process OM from SL and thrive on it even without additional input of N or bacterial culture.

The content of AHN, as can be seen from Figure 1b, depends directly only on N application, but MO contributed to its retention and preservation in the substrate – variant 5 (FS/SL + N) contains 196 mg/kg of AHN less than variant 6 (FS/SL + N + MO) at the 1<sup>st</sup> period. The change in AHN content by the end of the experiment is insignificant – for the variant 5 (FS/SL + N) AHN decreased by 6.7% relative to the initial value, for the variant 6 (FS/SL + N + MO) AHN value has not changed by the 8th period, although at the period 7 it was 6.9% lower than the initial value (Fig. 1b). Apparently, the consumption rate of MO for mineral nitrogen matched the intensity of their organic nitrogen mineralization process, allowing the initial level of AHN content to be maintained.

The pH of the medium has been increasing throughout the entire period of the experiment, from 2.8–2.9 pH up to 4.4 for FS for the variant 2 (FS/SL) and up to 4.3 pH for the variants 5 (FS/SL + N) and 6 (FS/SL + N + MO) (Fig. 1c).

The phytotoxicity test showed 100% germination of radish seeds (Table 3) with an increase in dry biomass growth in the following order: the variant 2 (FS/SL), the variant 5 (FS/SL + N), and the variant 6 (FS/SL + N + MO). The best result (82.35% increase in dry biomass)

was observed in the mixture (FS/SL = 1/0.5) + N + MO(Table 3). Obtained results were likely due to both the high content of AHN (406 mg/kg – the maximum value among the mixtures with SL) and the optimal ratio of available organic matter in the substrate, as it is confirmed by the comparison with the variant 12 (FS + N + MO) with 6.5% more AHN content (434 mg/kg) without SL, with less biomass growth (Fig. 1a and 1b).

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5.2. Soilgrounds with a FS/SL ratio of 1/1. Similar to mixtures with a FS/SL ratio of 1/0.5, after the addition of all amendments at the 1st period, the highest organic matter content was observed only in the mixture with SL (variant 3 - FS/SL). The organic matter content in the mixture with FS/SL + N + MO (variant 8) was lower (by 1.8%), and the lowest content (6.6% less than in variant 3 - FS/SL) was observed in the mixture with the only additive N (variant 7 - FS/SL + N) (Fig. 1a). After 82 days of composting (7<sup>th</sup> period), the organic matter content increased relative to the initial level by: 1.5% for the variant 3 FS/SL), 4.9% for the variant 7 (FS/SL + N), and 15.8% for the variant 8 (FS/SL + N + MO). 6 months after composting (8th period), the organic matter content decreased in comparison to the original levels across all variants by: 12.3% (variant 3 - FS/SL), 4.4%(variant 7 - FS/SL + N), and 4.5% (variant 8 - FS/SL + N) CSL + N + MO) (Fig. 1a). The amount of AHN in the 7 variant and the variant 8 (FS/SL + N and FS/SL + N + MO) with fertilizer application decreased by 22% and 50% respectively compared to the original levels (Fig. 1b). Obtained results indicate intensive processes of mineral nitrogen uptake for MO nutrition and an increase in their biomass. An increase in organic matter content within the composting process was observed in the variant 3 (FS/ SL) where no extra additives were applied, confirming the hypothesis proposed above about the interaction between MO inhabiting the original FS and SL (Fig. 1).

During the experiment, the medium's pH for FS increased from 2.8–2.9 to 4.5 in all experimental variants (Fig. 1c).

The phytotoxicity test showed a 100% germination rate for radish seeds, with the increase in dry biomass progressing in the following order: the variant 8 (FS/SL + N + MO), the variant 7 (FS/SL + N), and the variant 3 (FS/SL). Thus, the best result for the FS/SL ratio of 1/1 was obtained when radish plants were germinated in the presence of only SL in the mixture (50% increase in dry biomass) (Table 3).

**5.3.** Soilgrounds with a FS/SL ratio of 1/2. After adding all the supplements to the mixtures, the content of OM was decreasing in the following order at the 1<sup>st</sup>-term: FS/SL mixture (4<sup>th</sup> variant – 62.7%) > mixture FS/SL + N (9<sup>th</sup> variant – 54.4%) > mixture FS/SL + N + MO (10<sup>th</sup> variant – 53.8%) (Fig. 1a). After 82 days of composting (7<sup>th</sup> period), the organic matter content increased relative to the initial level by: 13.8%, 16.2%, and 20.6%



in each variant, respectively. 6 months after composting (8<sup>th</sup> period), the organic matter content decreased in comparison to the original levels by: 17.9%, 11.1%, and 1.4% relative to the original level in variants 4 (FS/SL), 9 (FS/ SL + N), and 10 (FS/SL + N + MO) (Fig. 1a). These results demonstrate that high initial organic matter content contributed to a more intensive growth of organic matter content during composting. Probably, this indicates a better development of microbial mass with an increase in the amount of OM for nutrition. Additionally, as for the mixtures with the ratio FS/SL - 1/1, the extra introduction of N contributed to the process of organic matter accumulation (Fig. 1a and 1b). In the mixtures with N introduction, the content of AHN decreased not only at the end of the experiment by 36.4% for the variant 9 (FS/ SL + N) and by 20% for the variant 10 (FS/SL + N + MO), but in 3 days of composting process (1<sup>st</sup> period), AHN content has already differed significantly between the variant 9 (FS/SL + N - 308 mg/kg) and the variant 10 (FS/SL + N + MO - 140 mg/kg) (Fig. 1b). This may indicate that for the ratio of FS/SL - 1/2, the amount of N was initially insufficient to maintain a higher level of AHN. At the 7th period, there was an increase in AHN content by 10% for the variant 10 (FS/SL + N + MO), but then it has decreased by the 8<sup>th</sup> period and reached 80% of the original value (Fig. 1b).

During the experiment, the medium's pH for FS increased from 2.8-2.9 to 4.7 in the variant 4 (FS/SL) and the 10th variant (FS/SL + N + MO), and to 4.6 in the variant 9 (FS/SL + N) (Fig. 1c).

The phytotoxicity test showed 100% seed germination for radish, and the biomass growth was increasing from the variant 4 (FS/SL) to the variant 9 (FS/SL + N), and then to the variant 10 (FS/SL + N + MO). Thus, the most successful result for the FS/SL ratio of 1/2 was achieved by germinating radish plants in the presence of FS/SL + N + MO in the mixture (dry biomass growth of 15.38%). Germination of radish plants in the presence of the FS/SL ratio of 1/2 showed the worst results among all variants (dry biomass growth of 8.33%) (Table 3).

The results obtained for the dynamics of organic matter content during the composting of SL correlate with the findings described by Davide Savy et al. [48]. In their experiment on composting with lignin-based additives to study microbial communities over a period of 180 days, the amount of organic matter initially was increasing and then was decreasing. It was concluded that there was a cessation of sufficient nutrition for the microbial organisms due to the humification of the organic matter and its transition into a less accessible form for decomposition. A similar dynamic of organic matter content can be assumed in conducting our experiment.

Thus, the obtained mixtures not only demonstrated the high content of organic matter and high AHN levels upon the addition of mineral fertilizers but also had a high probability of gradually transforming into humic acids, which are the basis of soil, albeit requiring further investigation. These mixtures, when utilized as an additive to the nutrient-rich topsoil layer applied on the surface of reclaimed anthropogenic disturbed lands, hold the potential to decrease the volume of soil required for restoration, and enhance its agrochemical properties. This is accomplished through the SL usage as a nanofertilizer, which can contribute to gradual release of carbon and nitrogen for nourishment of soil microorganisms and plants.

The study revealed patterns in the relationship between the initial components and their number to the final values of agrochemical indicators in the mixtures for reclamation of quarry dumps based on SL. It also enabled us to evaluate the processes occurring during the composting of these mixtures. Analysis of the results for phytotoxicity and agrochemical composition indicators showed prospective applicability of the obtained mixtures as additives to quarry dump material during reclamation process. The studied mechanisms of the components' interaction in the mixtures can serve as a basis for planning and developing new mixtures using the same components, but meeting predetermined final parameters. Therefore, the application of SL in the reclamation of technogenicaffected areas will contribute to waste disposal from the wood processing industry, provide a basis for the development and creation of soil-like bodies with predetermined properties, and allow its use as a nanofertilizer.

#### CONCLUSIONS

Variants combinations of fine fraction soil with sodium lignosulfonate at different ratios of sodium lignosulfonate (0.5, 1, and 2) in the absence extra additives showed organic matter content of 29.8%, 35.2%, and 44.8%, respectively. The addition of SL did not have any significant impact on the content of AHN. Alkali-hydrolysable nitrogen levels for all mixtures was being consistent with the content in fine fraction soil at 42 mg/kg.

When adding 1 gram of mineral nitrogen fertilizer to mixtures with a component ratio of FS/SL - 1/0.5, 1/1, and 1/2, the organic matter content increased up to 30%, 36.5%, and 43.3% respectively. The content of alkali-hydrolysable nitrogen was 196, 252, and 196 mg/kg respectively.

The addition of liquid bacterial culture in the presence of nitrogen fertilizer to the mixtures with sodium lignosulfonate under the same composting and drying experimental conditions resulted in the maximum increase in organic matter content for each of the FS/SL ratios: 33.2%, 41.2%, and 52.4%. The maximum value of AHN content was observed among all the studied mixtures for the variant FS/SL (1/0.5) + N + MO - 406 mg/kg.

Variants without SL addition, both in the presence or absence of nitrogen fertilizer, including the control vari-



ant, did not show significant changes in organic matter content and alkali-hydrolysable nitrogen content.

The medium reaction of all samples with SL content has increased by the end of the experiment (from the original level of FS 2.8–2.9 pH to 4.3–4.7 pH units) depending on the additives and their combination. The introduction of microorganisms into the FS without SL, both in the presence or absence nitrogen fertilizer, contributed to acidification to 4.0 and 3.6 pH units, respectively.

The conducted regression analysis of the obtained experimental data showed that the concentration of lignosulfonate has the greatest impact on the content of organic matter and soil acidity, while the application of nitrogen fertilizer affects the content of alkali-hydrolyzable nitrogen. The content of organic matter in the mixture increased in accordance with the composting period under sufficient moisture. Extra application of microorganisms and nitrogen fertilizer led to an increase in the content of organic matter, while the use of only nitrogen fertilizer contributed to a reduction in the amount of organic matter. Meanwhile, the content of organic matter and alkali-hydrolyzable nitrogen was decreasing over time, and the pH value was increasing.

The phytotoxicity analysis results of the substrate indicate a 100% germination rate of radish plants when germinated in the presence of all the obtained lignosulfonate mixtures. The best results in terms of germination rate and dry mass increase were observed with a mixture containing (FS/SL = 1/0.5) + N + MO (dry mass increase of 82.35% and 100% germination rate).

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Ekaterina S. Dorogaya, Elena V. Kuzina – conducting experiments. Ruslan R. Suleymanov, Maria G. Yurkevich – preparation of the article. Olga N. Bakhmet – general management.

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