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BOTTOM ASH UTILIZATION IN RECLAMATION OF DISTURBED TERRAINS

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Abstract

Utilization of different kind of waste in reclamation of disturbed terrains is main a part of Circular Economy concept. The use of the waste gives an opportunity to reduce the amount of generated waste and the areas disturbed by their disposal. All of it is key point for the conservation of environmental. Bottom ash utilization like a soil improver can reduse the amount of valuable waste with a hight content of organic matter and essential nutrients. This study aims to analise the possibilities for the use of bottom ash from biomass (straw) combustion for the reclamation of strongly acidic mine soils were studied. The ash shows hight potential for use on acid soils due the alkaline pH, high content of organic matter and nutrients - total N, P_2O_5, K_2O. Vegetation experiment with different bottom ash content is performed to be proven this possibility. The experiment shows that the addition of bottom ash leads to the neutralization of strongly acidic mine soils, but at the same time leads to salinization with an increase in the percentage of bottom ash. The optimum quantity of bottom ash for use is 5% of the amount of soil.

***Keywords**: Bottom ash; Mine soil; Reclamation; Soil improver*

Introduction

In the process of mining production are formed and rapidly increase areas disturbed by mining and storage of other waste. The embankments are characterized by a content of heavy metals and metalloids above the maximum permissible concentrations and pH in the acid range. It activates the processes of accumulation of the elements in the components of the ecosystems and of the migration from one component to another, thus the movement along the food chain is also realized. This provokes significant interest in developing technologies for their remediation, ecosystem restoration and their sustainable use [1-6].

The idea of a circular economy is becoming more widespread worldwide. This is based on the fact that the demand for raw materials and energy resources is growing daily, and many of them are in limited quantities [7].The effect of the extraction of these raw materials on the environment should also not be overlooked. On the other hand, the amount of a number of wastes is growing daily, and at the same time they can be a valuable resource in various industrial sectors. It has been proven that waste such as sewage sludge, fly ash, compost and others can be used as soil improvers in the reclamation of disturbed terrains [8-17].

In these cases it is necessary to introduce soil improvers to immobilize the pollutants - by raising the pH [1, 18, 19].

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Biomass bottom ash is waste that is retained in a kiln of the combustion plant of materials such as wood, straw and other parts of plants. Waste is characterized by higher porosity, permeability and high nutrient content. Biomass bottom ash is often used as a soil improver, as it is a valuable source of potassium (K), calcium (Ca), sodium (Na) and magnesium (Mg), as well as other macro- and micronutrients that are needed for complete plant development and growth. The chemical composition of bottom ash from biomass is usually dominated by the macronutrients Ca, K, phosphorus (P) and sulfur (S), as well as trace elements such as zinc (Zn), copper (Cu) and manganese (Mn), which allows its use as a soil improver [20-22].

An important quality of biomass bottom ash is the content of organic matter and phosphorus. It usually varies between 2 and 20% and contributes to increasing soil fertility. The use of biomass bottom ash would increase soil fertility and improve soil structure [23].

The high content of calcium compounds has a beneficial effect on the regulation of soil acidity. It is known that over time the solubility of calcium compounds decreases as a result of the slower release of the element and this prescribes a long-term effect on soil acidity[18, 21-24]. This would have a positive effect on soils with proven acidic pH - such as mining soils in the extraction of copper ores.

The present study aims to determine the possibilities for the use of bottom ash as a soil improver in the reclamation of mining soils in disturbed areas from copper ore mining.

Experimental

Materials

For the purposes of the present study, bottom ash obtained from the combustion of biomass (straw) in the production of ethyl alcohol was used. The ash is classified as waste with code 10 01 01 bottom ash, slag and boiler dust (excluding boiler dust mentioned in 10 01 04). At the time of the study, bottom ash was not used. It is transported to the landfill. Sampling of soil substrates from landfills for storage of mining waste from copper extraction was also performed.

Methods

The following parameters were tested in the bottom ash sample used for the vegetation experiment as a part of the present study: pH (H_2O) is definitely potentiometric; total nitrogen - by the method of Keldal; K_2O assimilable by Milcheva extraction and atomic emission spectroscopy; P_2O_5, by extraction by the method of Petko Ivanov and atomic emission spectroscopy with *Flavo* apparatus. The analyzes were performed in the Central University Laboratory at the University of Forestry. The same indicators were studied in the mining soil sample taken from the embankments.

Also, the bottom ash generator has provided additional research on the waste: phyto- and ecotoxicity test; Heavy metal content analysis; microbiological analysis; analysis of polycyclic aromatic hydrocarbons (surfactants) and polychlorinated biphenyls (PCBs) in pelta. The analyzes were performed at the Agricultural University, Plovdiv and SAA Nikola Pushkarov.

The possibilities of biomass bottom ash to be used as a soil improver are determined by conducting a vegetation experiment. Conditions - temperature and humidity are controlled conditions during the experiment. The vegetation experiment was carried out by mixing in different proportions of mining soils with bottom ash (5 and 15%) in containers with a capacity of 0.7kg. The experiment was performed in two replicates. The scheme of betting on the vegetation experience is presented in Table 1.

Table 1. Vegetation experience betting scheme

Variant / Component	Control sample	Biomass bottom ash content	
		5 %	**15 %**
Mine soil, кg	0.500	0.475	0.425
Biomass bottom ash, кg	0.000	0.025	0.075

At the beginning of the vegetation experiment, 30 seeds of the selected indicative species - *Lolium perenne* L. were sown. The duration of the vegetation experiment is 34 days. During this period, daily visual observations of the growth of the indicator species were carried out. At the end of the vegetation experiment, the changes that occurred in the substrates in terms of active soil acidity and electrical conductivity as a result of the applied bottom ash were studied. The number of sprouted plants and their development - length of underground and aboveground part are analyzed.

The analysis of data on soil acidity was performed according to Malinova in 2010 [25], humus content, basic nutrients, macro and micro-elements - according to ICP Forest in 2021 [26].

Results and discussion

Composition of bottom ash

Data on the physical and chemical characteristics of biomass bottom ash are presented in Table 2**.**

Table 2. Physical and chemical parameters of biomass (straw) bottom ash

Indicator	Unit	Value
pH	-	10,7
Electrical conductivity	μS/cm	2650,0
Dry matter / moisture	%	28,8 / 71,1
Organic matter	%	9,7
Total nitrogen	mg/kg	977,1
Total phosphorus	mg/kg	25549,56
Total potassium	mg/kg	25622,0
Calcium	mg/kg	144,4
Magnesium	mg/kg	7320.0
Copper	mg/kg	12,8
Iron	mg/kg	114.0
Zinc	mg/kg	28,0
Manganese	mg/kg	182,4
Lead	mg/kg	6,1
Cadmium	mg/kg	< 1,0

The data in Table 1 show that the studied biomass bottom ash has an alkaline reaction. This creates a prerequisite for its use in acidic soils. It is assumed biomass bottom ash will regulate an unfavorable (acidic) soil reaction, which negatively affects the growth and development of plants [24]. Despite the high content of alkaline earth elements, the biomass bottom ash has an electrical conductivity of 2650μS/cm. That does not imply a risk of salinization in the soils in which it is applied.

Biomass bottom ash has a high content of organic matter - 9.7%, which makes it a suitable ameliorant for the treatment of low-yielding soils - poor in humus and nutrients. The studied waste is characterized by a high content of nitrogen (977.1 mg/kg), which makes it suitable for use in low-yielding soils, such as those in embankments. Nitrogen is an essential nutrient and a component of many organic compounds in plants. In the reclamation of disturbed terrains, it is a limiting factor for the restoration processes [24-25].

The studied waste is characterized by a very high content of phosphorus (25549.5mg/kg) and low potassium (144.4mg/kg). Compared to medium or poorly stocked soils of phosphorus and potassium, the studied waste is several times higher than the stock of these elements [25]. The high content of phosphorus is expected to lead to positive changes in the composition of soil substrates. In the first place, it is an essential nutrient. The element is also involved in the immobilization of heavy metals and metalloids, such as those characteristic of mining soils in disturbed areas of copper mining. With regard to potassium, it is known that the function of the element in the plant organism is multifaceted. This element participates in the regulation of the physiological state of cellular colloids, activates the activity of various enzyme systems, participates in the processes related to energy transformation and nitrogen exchange, etc. [24].

Biomass bottom ash is with a very high content of magnesium (7320.0mg/kg) and low content in calcium (144.4mg/kg). The content of both elements is the cause of the alkaline pH of ashes and suggests that embedded in acidic soils - they would increase their pH [24 – 25, 27-28].

The biomass bottom ash also contains trace elements copper (12.0mg/kg – medium content), iron (1147.0mg/kg – low content), zinc (28.0mg/kg – low content) and manganese (182.4mg/kg – medium content), which are important for the growth and development of the plant organism. The presence of these elements is important for plant organisms. They take an active part in the oxidative-reduction processes of photosynthesis, respiration, biosynthesis of proteins and chlorophyte and others [24, 26].

The content of lead (6.1mg/kg - low content) and cadmium (<1.0mg/kg - low content) in biomass bottom ash is in very low concentrations. The addition of ash does not imply a risk of contamination with these elements [24, 26].

Agrochemical analyzes of the content of digestible macro- and microelements made in the Central Laboratory of the Institute of Soil Science "Nikola Pushkarov" confirm that the content of magnesium and calcium is a prerequisite for the use of biomass bottom ash as an ameliorant for acidic soils, due to expectations to increase their pH. Studies show that biomass bottom ash is rich in essential nutrients, and contains nutrients macro- and micronutrients in optimal proportions for vegetation development. According to the study, the ash does not contain chlorine compounds.

Table 3. Agrochemical indicators of the materials used for conducting the vegetation experiment

Variant / **Component**	pH (H_2O) -	Electrical conductivity	N %	P_2O_5 mg/100g	K_2O mg/100g
Mine soil, кg	3,6	0.956	0,089	0,5	2,0
Biomass bottom ash, кg	10,0	2.6	0,193	532,5	6979,8

Change in active acidity and electrical conductivity

Mining soils are characterized by an extremely acidic reaction, low nitrogen content, and very low content of digestible phosphorus and potassium. This pH range is an indicator of increasing the intensity of destructive changes in them and is caused by the high content of total sulfur in them. Conditions for plant nutrition are unfavorable. High acidity is the reason for the lack of bases. Nutrition is characterized by the absorption of excess micronutrients. In biomass bottom ash, the active acidity is strongly alkaline, with a high nitrogen content and a very high content of digestible forms of phosphorus and potassium [25-27].

Data on the change in active soil acidity after the end of the vegetation experiment are presented in figure 1.

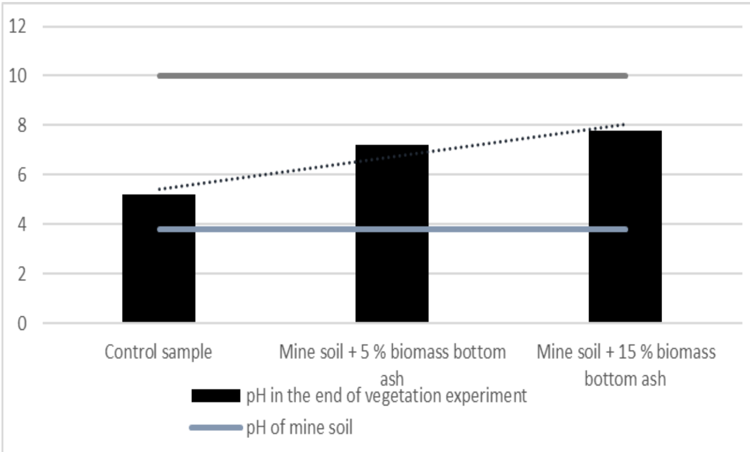

Fig. 1. Active soil acidity of the studied substrates at the end of the vegetation experiment

The data presented in figure 1 show that with increasing amounts of bottom ash, an increase in the active acidity in the substrate is observed. In the control sample, the active acidity is moderately acidic, in the variant with 5% bottom ash content the reaction is neutral, and in the variant with 15% bottom ash content it is slightly alkaline. This property of bottom ash is extremely important and shows that its use would lead to the neutralization of acidic substrates in the reclamation of disturbed terrain.

Data on the change in electrical conductivity at the end of the vegetation experiment are presented in figure 2.

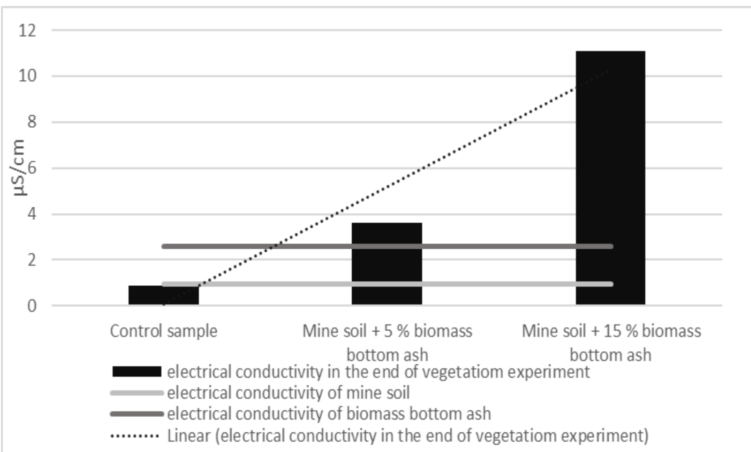

Fig. 2. Electrical conductivity of the studied substrates at the end of the vegetation experiment

The data presented in figure 2 show that the electrical conductivity increases with increasing bottom ash content in the tested samples. The substrates in the control sample and the variant with added 5% biomass bottom ash are unsalted, the variant with 15% bottom ash content is moderately saline. This is probably due to the high content of magnesium and calcium imported with the biomass bottom ash.

During the vegetation experiment the seeds germinate first in the version with 15% biomass bottom ash content (2 days after sowing), then the seeds in the control sample and in the version with 5% ash content (3 days after sowing). A probable reason for the faster germination of seeds in the variant with 15% biomass bottom ash content is an increase in pH after application of the ash.

Results from the development of the indicator species during the vegetation experiment are presented in figure 3. As can be seen from the figure, although the seeds in the version with 15% biomass bottom ash germinate faster, they have slow growth. The seeds in the control sample germinate at the same time as the seeds of the 5% biomass bottom ash variant. However, the plants from the variant with added biomass bottom ash grow faster and visibly the amount of biomass formed by them is greater. This is probably due to the fact that the acidity in the control sample is strongly acidic, and the application of bottom ash helps to regulate the acidity and create optimal conditions for plant development. At the end of the vegetation experiment (week IV) the best growth ability was shown by the grasses in the pots with 5% content of biomass bottom ash, followed by the grasses planted in the control sample. In the variant with 15% content of biomass bottom ash, difficult development of the indicator species is observed, as in one of the repetitions the plants gradually die and at the end of the experiment there are no survivors. The probable reason is the established salinity.

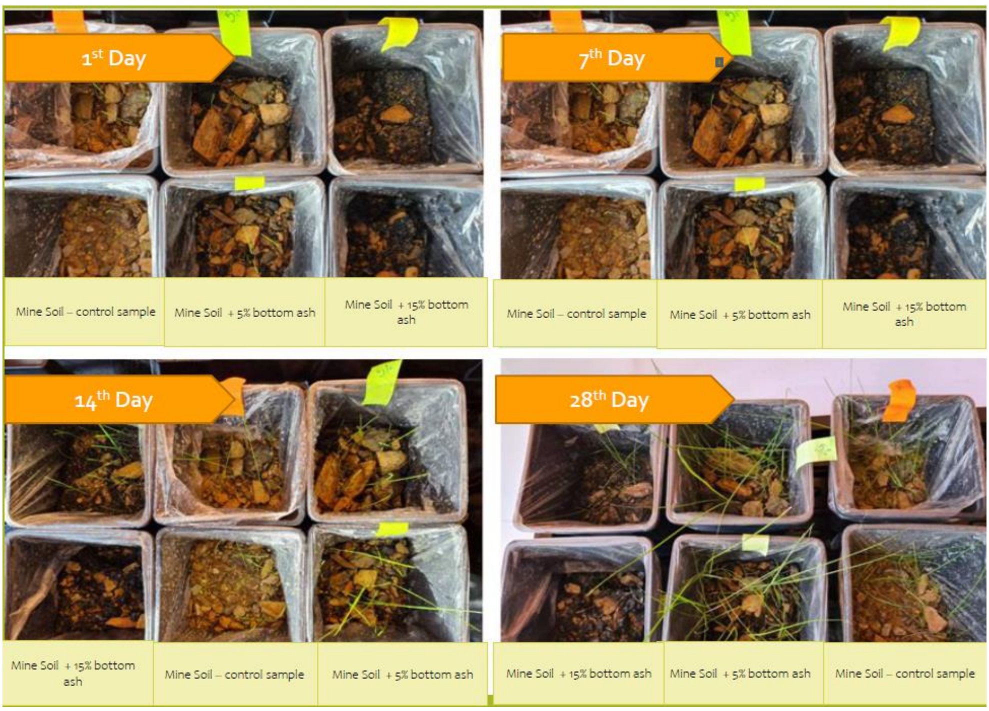

Fig. 3. Development of the indicator species for 1 month

Analysis of biometric indicators

At the end of the vegetation experiment the plant species were eradicated and the following biometric indicators were reported: percentage of sprouted plants compared to sown, length of the aboveground part, length of the underground part of the plants and mass of the formed biomass.

Percentage of sprouted plants

At the end of the vegetation experiment, the percentage of germinated seeds compared to sown was calculated. As mentioned above, 30 ryegrass seeds were sown in each pot at the beginning of the experiment. The data are presented in figure 4.

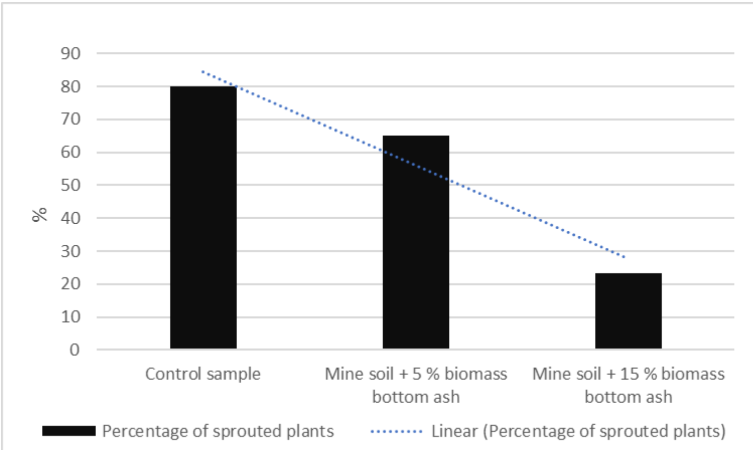

Fig. 4. Percentage of sprouted plants

As can be seen from figure 4 with increasing the amount of biomass bottom ash the percentage of sprouted plants decreases.

The maximum amount of germinated plants was observed in the control sample, followed by the variant with 5% biomass bottom ash content. In the variant with 5% biomass bottom ash content the sprouted plants are 15% less compared to the control sample, and in the variant with 15% bottom ash content they are 57% less compared to the control The graph shows that the increased amount of biomass bottom ash (15%) has an inhibitory effect on germination, probably due to high electrical conductivity and salinization. 5%.

Biometric indicators

Development of the studied indicator species is presented in figure 5.

The data presented in figure 5 show the difference in grass species at the end of the growing season experiment in all variants. Better growth is observed in the grasses grown in the variant with 5% biomass bottom ash content, followed by the plants in the control sample. In the version with 15% biomass bottom ash content, the development of grasses is the slowest. In one of the repetitions until the end of the vegetation experiment, complete extinction of the sprouted plants was registered, probably due to the established salinization.

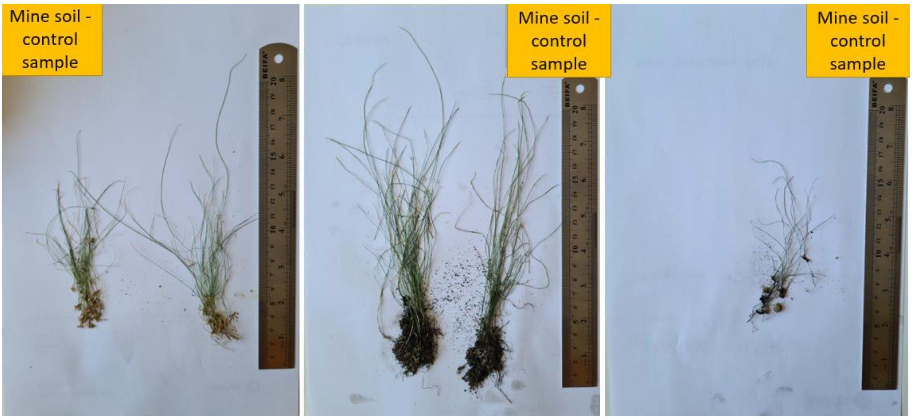

Fig. 5. Development of cultivated grasses at the end of the vegetation experiment

Length of aboveground and underground part (cm)

Data on the biometric indicators for the length of the aboveground and underground part of the plant are presented in figure 6.

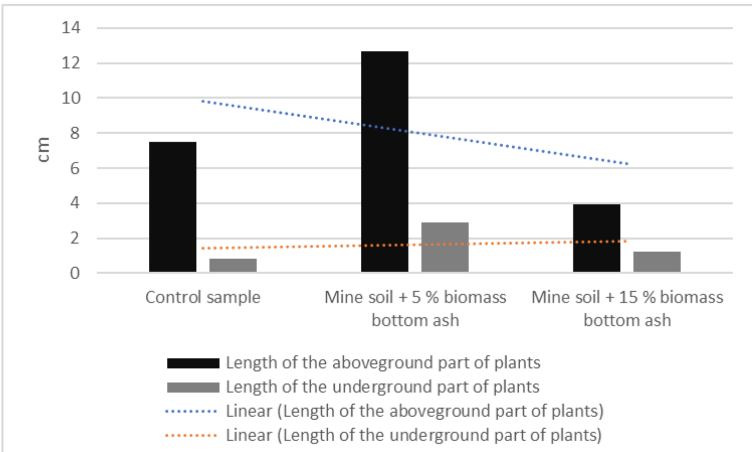

Fig. 6. Biometric indicators - length of the aboveground part and the underground part (cm)

The greatest length of the aboveground part is formed by the plants of the variant with 5% biomass bottom ash content. The data clearly show the tendency to decrease in size with increasing the amount of bottom ash applied in mining waste. The smallest length is formed by the grasses in the variant with 15% biomass bottom ash content. As can be seen from the graph, the length of the aboveground part in the variant with 5% biomass bottom ash content is 0.59 times longer than the control, while in the version with 15% biomass bottom ash content he aboveground part of the grass is 3.25 times shorter than the control. The results show that the optimal amount of bottom ash for application on mining waste is 5%. This amount achieves alkaline pH, which improves plant nutrition on the one hand, and on the other hand imports the required amount of nutrients. The higher amount of biomass bottom ash inhibits the growth of grasses, probably due to the alkaline pH and the large amount of alkaline earth elements, which may be the reason for the immobilization of trace elements in the substrate

The length of the root system of Lolium perenne L. in the variant with 5% of the biomass bottom ash content is greater (2.9cm) than in all other variants, as shown in Fig. It is followed by the plants from the variants with 15% content of biomass bottom ash - 1.2cm. The smallest length of the root system is observed in the control sample.

As can be seen from the graph, the application of bottom ash in Series II has a positive effect on the development of the root system. This is due to the introduction of nutrients - especially phosphorus and potassium, which are responsible for the formation and development of the root system in young plants.

Amount of biomass

To determine the amount of biomass formed during the experiment, the mass of plant biomass at the end of the vegetation experiment (after drying the grass). Data on the amount of biomass formed are presented in figure 7.

As can be seen from figure 7 the largest amount of biomass is formed in the variant with the addition of 5% biomass bottom ash. In the same variant the greatest length of the above-ground and underground part of the cultivated plants was measured. This is probably due to the increase in the pH of the acid waste, as a result of which the plant feeding conditions are improved. As mining waste is poor in nutrients - imported bottom ash probably increases their content, and elevated pH leads to immobilization of heavy metals characteristic of them. Despite the lower number of sprouted plants in the 5% biomass bottom ash variant compared to the control, the amount of biomass formed in the 5% biomass bottom ash variant was 0.8 times higher.

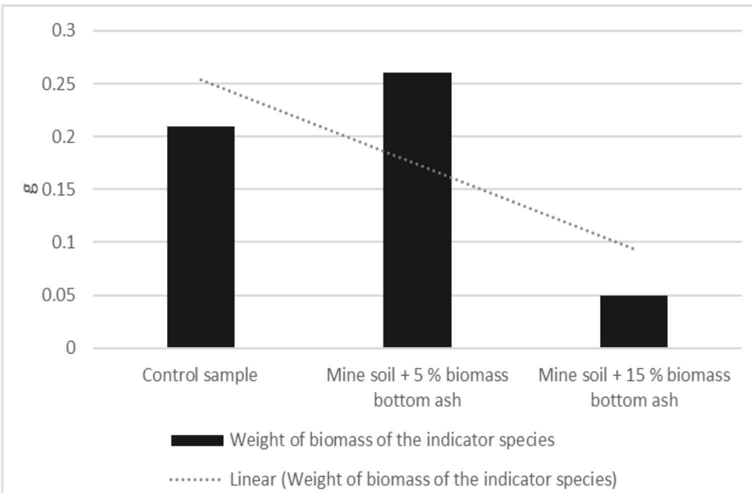

Fig. 7. Quantity of biomass of the indicator species, g

As the biomass bottom ash content increases, the amount of biomass formed decreases. The probable reason for this is the strongly alkaline pH and the established salinization, which lead to a slowdown in plant growth.

These results suggest that biomass bottom ash used in an amount of - 5% leads to improved growth environment in acidic substrates - helping to regulate pH, introduction of nutrients - phosphorus and potassium, improving plant nutrition conditions and immobilization of possible contaminants.

Conclusions

The study found that the bottom ash of straw generated in the production of ethyl alcohol can be used as soil improvements in the reclamation of disturbed terrain.

It was found that the application of bottom ash in mining soils leads to an increase in its acidity, in direct dependence on the content of bottom ash.

It was found that with increasing bottom ash content, the electrical conductivity in the studied samples also increases. At 15% bottom ash content, salinity of the substrates was observed.

The optimal amount of bottom ash to be added to mining soils is 5%. In these variants the formation of the largest amount of biomass with the longest underground and aboveground part is established.

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