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Land Cover Pollution from Mining and Metallurgical Enterprises and Biotechnological Method of Remediation Using Biochar

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Abstract

Sources of pollution have been identified, the emission zone of influence of the city Ridder zinc plant, East Kazakhstan Region (EKR), area of distribution of pollutants. Condition of soil and vegetation areas are around the zinc plant. Studies have shown a negative impact on soil and vegetation. Thus, a significant area of soil adjacent to the zinc smelter, subject to erosion processes. Erosion manifests itself in the form of runoff from the soil surface, the formation of deep furrows and gullies. The surface of the soil over a large area devoid of vegetation. Analytical data is possible to determine the content of heavy metals in the soil as a gross, and their mobile forms. Priority pollution elements are zinc, lead, copper and cadmium. Concentrations of heavy metals in the soil exceeds the Limit Accessible Concentration (LAC) as the gross and mobile forms. The accumulation and distribution of heavy metals in the vegetative parts of trees and shrubs different. The vast majority of plants is in a depressed state. Under the influence of toxic emissions on the leaves are formed burns, there is drying branches and axial crop shoots, weakened vegetative and generative development. To reduce the negative impact on the soil and the plant has been used biochar based on rice husk as meliorant improving important soil properties and sorbent of heavy metals, selected more resistant trees and shrubs to restore the soil and vegetation.

Keywords: Accumulation; Biochar; Carbonation; Erosion; Heavy Metals; Migration; Pollution; Sorbent

Introduction

Degradation and soil pollution - a result, mining operations, agricultural production, natural phenomena (landslides, mudflows, floods, forest fires, haphazard deforestation, accidents in factories, waste pollution and abandoned ordnance former military sites, etc.). Kazakhstan has acquired special urgency of the above factors. Resource-rich mineral wealth of the republic developed in all regions of mining or open pit. This disturbed soil and vegetation areas, sometimes going their complete destruction. These areas are infertile, often toxic, not overgrown for a long time, exposed to erosion and degradation processes with the deterioration of the environment, causing significant damage to human health. In this case there is an imbalance in the functioning of the biosphere, the main part of the existence of life on earth. According to the Agency of Land Resources (2011) on the qualitative characteristics of the land in the East Kazakhstan region technologically-impaired disturbed land is 14,018 hectares, waste land - 6702 thousand hectares.

Materials and Methods

Object of research are the areas under the influence of emissions of the processing mining Ridder of the East Kazakhstan region. Effect of zinc, lead factories of the surrounding landscapes. Zinc and lead plants are located in the city.

Methods

Field and laboratory analysis. Reconnaissance detour the territory, the definition of pollution sources. Effect of industrial emissions on land cover on eroded processes by external characteristics of plants, their death and absence. Determination of physical properties, the chemical composition of the soil produced by conventional methods in soil science. Determination of heavy metals and other chemical elements in the soil, soils, plants were conducted nuclear physics and atomic absorption methods. Carbonization was carried rice husks in a screw reactor. The process of carbonization of samples was carried out under isothermal conditions. Modifying the samples were in a rotating reactor in an inert atmosphere with argon flow rate of 50 cm3/min [1].

The structure of biochar and sorption properties are determined by electron microscopy. Spectral analysis of the chemical composition of biochar and electronic microanalysis soil in order to detect adsorption of heavy metals (Zn, Pb), on the electron probe micro analyzer Superprize 733 Dzheol company (Japan).

Results and discussion

Emissions of zinc plant a negative impact on the environment. Disturbed soil cover, vegetation is destroyed and formed eroded areas, failures. The impact of emissions zinc plant spreads over long distances. The area of distribution of the plant emissions of the circle is 2 km away, with a particular impact on the wind rose in the east of the plant to the town and the hilly mountains, which is devoid of vegetation and is dissected by erosion furrows and gullies Figure (1a, 1b). Within a radius of 2 km is heavily plant emissions impact on land cover. So, at the plant emissions impact of gullies formed, grooves, ditches, there is a continuous flushing of the upper layers of the black earth soil.

Figure 1(a-b): Soil of Around the Plant (a) Erosion Process Vegetation (b) Soil Without Vegetation.

Around concentrators due to soil contamination area devoid of vegetation. The peculiarity of emissions of non-ferrous metallurgy is the simultaneous presence of these large amounts of heavy metals. Most, Dangerous for the environment constitute a group of heavy metal toxins that accumulate in the soil and plants.

According to the results of our research in zinc plant location area it found that the content of total lead in the upper 10cm soil layer exceeds MPC by 1.68 times. Zinc - at 25.46 times, copper - in 1054.6 times, cadmium - to 440.9 times, especially the middle and lower part of the site heavily contaminated with heavy metals, as the area has a large slope to the river Silent. Geochemically anomalous regions in soil containing a significant amount of the chemical elements. Many plant species are adapted to such conditions, but when the plant and the environment affect man-made emissions of mining plants and enrichment plants over large areas of soil cover is deprived of vegetation and tree cover. Emissions of non-ferrous metals are transported over long distances. Marked accumulation of heavy metals in the soil and plants in the region of 10 - 15 km or farther from the source of contamination.

Plants - one of the most sensitive indicator of anthropogenic environmental changes. They show changes in the environmental conditions under the influence of different factors, and therefore widely used in the evaluation of environmental pollution. The vegetation cover is under intense anthropogenic pressure of pollutants from the air and contaminated soil. Some of them are required for metabolic processes in plants, but an increase in their concentration becomes toxic for the plants, other metals such as Pb, Cd, and so on. G., Toxic, even in low concentrations [2]. According to some sources, the pollution of meadow vegetation Pb and Zn is fixed at a distance of 12 km from the lead-zinc enterprises [3]. Near Zinc Plant (1 km), the accumulation of these metals in the soil is so great that the cultivation, any crops for animal feed or for taking their food is harmful to human and animal health.

Heavy metals are strongly adsorbed and interact with the soil humus, form sparingly soluble complexes. Thus, there is their accumulation in the soil. In addition, the soil under the influence of various factors, there is a constant migration of substances falling into it and carrying them long distances [4]. Heavy metals in the soil falling emission enterprises are firmly bonded in the top layer. The maximum content of metals in soils is observed at distances of 1-3 km from the pollution source [5]. Less resistant to his excess crops, resistant - legumes. The least resistant to contamination with lead plant species are maple, onion and cocksfoot. The lead concentration above 10 mg/kg dry weight is toxic to most crops. Several authors found a slight ion uptake by plants such as Cd, Br, Cs, while Pb slowly enters other heavy metals in plants and transported to the ground organs [6,7]. Different types of plants have unequal ability to accumulate lead, that is widely used to reduce the adverse impact on the urban plant communities and use them as a promising battery - phytoremediation.

Our data show that at the site of shrubs (lower part) Pb content exceeds the MPC in 1241 again, Zn - in 781 times, Cu - 11 times, Cd - 2695 times. In the middle part of the plot in the poplar plants Pb content exceeds the MPC in 1580 again, Zn - in 317 times, Cu - 5 times, Cd - 1345 times. The upper part of Pb in site pine plants MPC exceeds 670 times, Zn - 298 times, Cu - 5 times, Cd - 1,197 times. Research on the content of heavy metals showed that plants growing on control sites located 25 km to the north of the plant, the excess of heavy metals of Pb in herbs -to 2.8 times, Zn - 3.3 times, Cu - 0.6 times, Cd - 3,3 times. In the bushes - Pb 5.8 times, Zn - 3.6 times, Cu - in 0,4 times, Cd - 7,7 times. When the content of soil in the 100-500 mg/kg of lead old leaf curling occurs [8]. In the experiments to reduce the impact of heavy metals in the soil and the plant has been used biochar. It was obtained from the pyrolysis of rice hulls at (450˚C).

To test biochar as a sorbent of heavy metals was laid on the site of field experience intense accumulation of pollutants and were planted shrubland culture of the local flora. The soil cover of the experimental plot was plowed in, depending on the root system of planting holes for trees will be at least 60 × 60 × 100 cm, shrubs 30 × 30 × 50 cm. Under the trees were added 1.2 kg of biochar, under the high bushes of 0.9 kg under low shrubs 0.6 kg of biochar. By planting herbs and mixtures of 30 kg per 100 m^2. Descriptions section showed that the natural flora is limited to two or three species, and in some areas formed monotsenozy. The vast majority of plants is in a depressed state. Under the influence of toxic emissions on the leaves are formed burns, changing life-form in the direction of reducing the habit, there is drying branches and axial crop shoots, weakened vegetative and generative development.

It is known that biochar, when applied to the soil improves soil properties and retains elements of fertility. Many scientists from the literature suggest that the use of biochar has a positive effect on the properties of the soil fertile [9]. Thus, the low fertility of the soil is worrying about the sustainability of agriculture in the regions dominated by oksisoli. Using mulch, manure and compost increases soil fertility in tropical conditions, short-term, as the organic material is rapidly oxidized and leached quickly added base. Adding biochar to infertile oksisoli provide long-term improvement of soil fertility. [10] Biochar originally consisting of single and fused "C" aromatic ring has a large surface area per unit weight and high density [11]. Because of these properties, biochar is a great rekaltsitrantom in tropical soils and makes a great ability to absorb cations per unit weight than biogenic soil organic matter. The use of biochar in soils is not a new concept. For example, in the Amazon Basin, anthropogenic dark soils contain large amounts of charred materials that have been added to the pre-Colombian farmers [12], who used logging residues and other carbon in agriculture. In such soils, biochar acts as meliorant soil, improving soil physical properties and efficiency of nutrient use. In order to predict the reactivity of biochar and stability, it is important to know the organic structural composition. Biochar from the soil of the Amazon region consists of highly heterogeneous mixture of organic structures. The structural form of "C" in biochar is dependent on the biogeochemistry of biomass feedstock and pyrolysis conditions [13]. Biochar, initially consisting of the condensed aromatic "C" remains in a soil environment Millennium biochar whereas with higher aliphatic and aromatic single ring "C" will mineralizovyvatsya faster. The surface area and density of biochar has a great influence on the absorption capacity of the soil and fertility. It is important from what is biochar elements. Thus, the spectral analysis of biochar produced from shell pecans showed that it is enriched with C, Ca, K, Mg, N Si, and the soil of the coastal plains of South Carolina consisted of. Al, Fe, Na, Si. Pyrolysis of organic material at 400-700˚C to a concentration "C", but to decrease and H by evaporation of adsorbed H_2O. Structures containing biochar in N, such as amino acids, amines, amino sugars at high temperature pyrolysis (700˚C) were possibly in the form of Heterocyclic fused aromatic structures. Thus, most of the N in the biochar was present in the form of heterocyclic N rekaltsitranta often than bioavailable amine N. [14]. Scientists from the US state of South Karalyn conduct experiments to improve and maintain lung soil fertility by adding various concentrations of biocharpecans and learn positive results [15]. It is noted that the high stability of biochar in the soil is a charity in the sequestration of carbon into the atmosphere. Chemical composition of raw material for carbonization - rice husk composed of silica and organic substances (Table 1).

Raw materials	Content %								
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	Organic compounds
Rice husk	0,61	15,64	0,24	0,12	0,45	0,18	0,48	0,28	82

Table 1: Chemical Composition of Rice Husk

Organic matter in the rice husk comprise 82%, and silica - 15.64%. The rice husk ash contains mainly silica (86.48%). Composition rice husk cellulose fiber represented the main component of cell walls and lignin - polymeric organic compound (Table 2).

No	Composition	Content
1	Water	3,75- 24,08
2	Ash	11,86-31,78
3	pentosan	4,52-37,0
4	Cellulose	43,32-43,12
5	lignin	19,20-46,97
6	Protein	1,21-8,75
7	Fats	0,38-6,62

Table 2: Rice Husk's Main Component.

"Nano karbosorb" - activated charcoal - porous carbon body, grained and powdery, developing upon contact with gaseous or liquid phases of a significant surface area for the flow of sorption phenomena. Useful properties of coal were known in ancient Egypt, where charcoal is used for medical purposes is already 1.5 thousand. BC The ancient Romans also used charcoal to purify water, beer and wine. Currently activated carbons occupy a leading place among the filtering materials. Application of activated carbon greatly expanded. Activated carbons have an important role in protecting the environment. "Nano karbosorb" has a high surface area, thereby absorbing (adsorbing), many substances (especially well hydrocarbons and their derivatives, weaker - alcohol, ammonia, water and other polar substances). Very finely activated carbon is produced by thermal decomposition (carbonization without air) some polymers.

Pore sizes ranging from 1,6 nm (the specific surface area is 1000 m^2/g) or more to 200 nm (specific surface area of about 1 m^2/g). Finely activated charcoal well adsorbs, even at low concentrations or small partial vapor pressures. For shirokoporistogo activated carbon is characterized by the phenomenon of capillary condensation. The pore structure: The activated charcoal has distinguished three categories: micro, meso and macro-pores. Micro- and mesopores account for the largest part of the surface of activated carbon. Accordingly, it is they who contribute most to their adsorption properties. Micropores are particularly suited for adsorption of small molecules and mesopores - adsorption of larger organic molecules.

Decisive influence on the pore structure of activated carbons have the raw materials for their production. According to the results of experiments, the effect on the ability of the soil substrate to retain nutrients biochar, due to the fact that the morphology of biochar has a complicated porous structure, characterized by a great variety of forms. Biochar was examined with a transmission electron microscope. (Figure 2) shows images of the surface of sorbents based on RSH at different temperatures and carbonation) initial rice husk; b and c, d, e, f) in the pyrolysis 450°C.

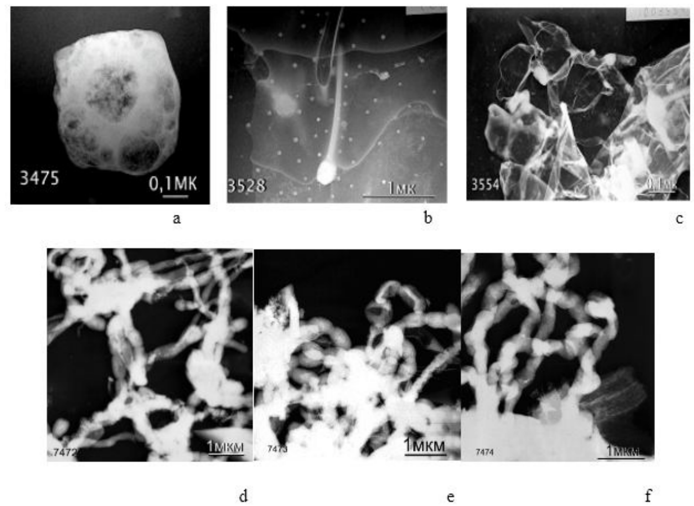

Figure 2: Electron Micrographs of the Sample RSH-450°C.

From electron microscopic image of the original sample RSH it shows that the sample consists of various kinds of carbon particles: carbon fiber consisting of rounded particles, ellipsoidal particles and denser carbon structures. In the process of carbonization increases pore size varies sorbent structure is synthesized. Electron microscopic studies have shown the formation of the morphology and structure of biochar. The biochar structure there are a large variety of morphological forms of the thin membrane films to nano-sized carbon fiber. Adding biochar to the soil enhances its fertility by raising the exchange capacity for cations. Increasing the cation exchange capacity is due to the carboxylate groups on the surface of the biochar, as well as organic acid carboxylate groups adsorbed biochar.

Foreign researchers have shown that the use of biochar obtained at temperatures of 300-400°C takes precedence when applied to the soil to improve its fertility. High pyrolysis temperature (700-800°C) may affect the relatively low level of biochar oxidation and thus the lack of a significant effect of supplementation on its exchange capacity for cations. The higher the pyrolysis temperature usually cause condensation of aromatic structures and even the formation of graphitic nuclei. Such highly condensed aromatic carbon has a smaller surface area and fewer oxidizable functional groups are more open than (less than fused) aromatic carbon structure. High-temperature biochar also more resistant to chemical oxidation and microbial. Rekaltsitratnye characteristics of high-temperature biochar would be a desirable feature when removing atmospheric CO_2 and carbon storage in the soil [16]. Our main goal here is to increase the exchange capacity for cations values can therefore be assumed that the addition of biochar obtained by low-temperature pyrolysis, more preferably to increase soil fertility.

Research based biochar rice husk revealed that may be obtained by carbonizing a developed structure with a larger specific surface and porosity, which improves its sorption properties. For example, electron-microscopic studies and spectral analysis of soils contaminated with zinc smelter emissions shown in the control variant there is zinc, and the version with biochar in the elemental composition of the zinc is present in (Table 3) (Figure 3 a, b). Thus, spectral analysis indicated the sorbent properties of biochar.

Elements	Wt% Mass fraction (control option)	Wt% Mass fraction (variant using bio carbon)
C	12.12	13.62
O	48.75	43.78
Na	1.13	2.95
Mg	1.17	0.92
Al	6.87	6.03
Si	22.55	20.51
K	1.70	1.52
Ca	0.69	0.55
Ti	0.64	0.50
Fe	4.39	5.13
Zn	**-**	**4.49**

Table 3: Spectral Analysis of the Soil on the Variant of the Experiment.

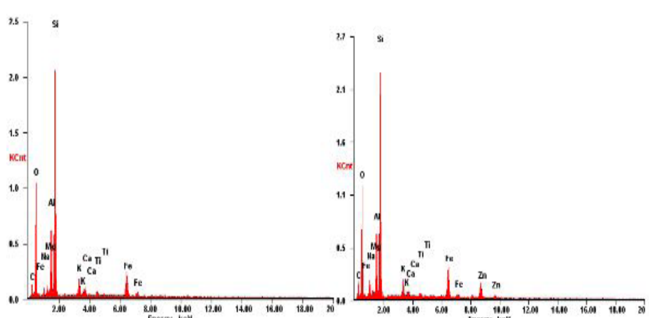

Figure 3(a-b): Elemental Composition of Soil a) control Option b) Using Biochar Option.

In variants of the experiment for the rehabilitation of contaminated soil emissions of zinc plant was made electronic microanalysis soil monitoring and the version with biochar, in order to detect adsorption of heavy metals (Zn, Pb), in electron probe microanalyzer Superprob 733 Dzheol company (Japan). The results showed only adsorbed zinc, but not lead sorption detected. Perhaps this is due to the temperature pyrolysis produce biochar. (Figure 4 a,b) clearly shows the biochar with a vivid manifestation of the structure. The National Nanotechnology Laboratory performed open-electron microscopy and elemental analysis of soil incubated biochar. soil structure Snapshots control samples and samples with biochar based soil sampling depth performed on an electron microscope SEM Quarta 3 D 200i.

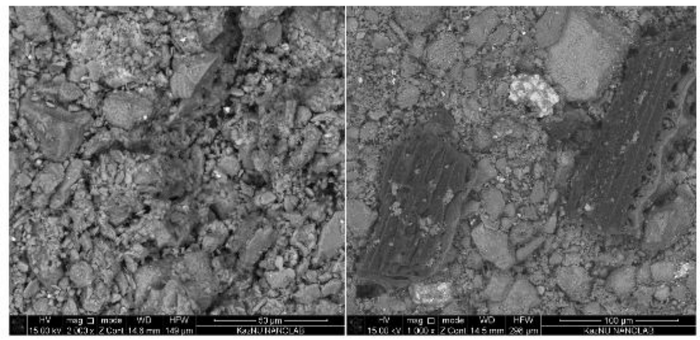

Figure 4(a-b): Experimental Plot (Black Earth Soil Contaminated with Zinc Smelter Emissions) a) Control Without Bio Carbon b) With Carbon.

To test biochar as a sorbent of heavy metals was laid on the site of field experience intense accumulation of pollutants. The soil cover of the experimental plot was plowed in, depending on the root system of planting holes for trees will be at least 60 × 60 × 100 cm, shrubs 30 × 30 × 50 cm. Under the trees were added 1.2 kg of biochar, under the high bushes of 0.9 kg under low shrubs 0.6 kg of biochar. By planting herbs and mixtures of 30 kg per 100 m^2. Descriptions section showed that the natural flora is limited to two or three species, and in some areas formed monoceros. The vast majority of plants is in a depressed state. Under the influence of toxic emissions on the leaves are formed burns, changing life-form in the direction of reducing the habit, there is drying branches and axial crop shoots, weakened vegetative and generative development.

Studies on the survival fitomeliorantov in extremely harsh environmental conditions, the impact of the mining industry showed that biochar improves soil environment and, to some extent serves as a barrier to the entry of heavy metals in the roots of plants. It noted the selective effect of biochar on the survival rate, the nature of the vegetation development and morpho-physiological indicators of established plants, enhancing their overall resistance to a complex of negative external factors. Sorption barrier biochar carbonized rice husk positive impact on the survival of maple yasenelistnogo- *Acernegundo* L., Fieldfare ryabinolistnogo- *Sorbaria sorbifolia* (L.) A. Br., Lantsetnogo- ash *Fraxinus lanceolata* Borkh., Turf belogo- *Swida alba* (L.) Opiz. Relatively better morphological and physiological indicators showed at povisloy- birch Betula pendula Roth, lilac amurskoy- *Syringa amurensis* Rupr, yagodnoy- apple *Malus baccata* (L.) Borckh., The Hungarian lilac -*Syringa josikae* Jacq. fil. and Wolf-lilac *Syringa wolfii* Schneid.

The plants absorb from the surrounding environment practically all chemical elements. The ash composition of man-made landscapes plants shows that different parts of the plants absorb and accumulate certain chemical elements. Thus, litter and roots of grass plants have the highest priority and the ash in the ash chemical element are silicon, calcium, sulfur, phosphorus, potassium, magnesium, nitrogen contained minimal. Timbers have a lower ash content. The composition of the ash depends on the growing conditions of the environment as herbaceous and woody plants. [17] The study found that the main sources of pollution is a zinc plant. The factory emission zone of influence manifest erosion of the soil in the form of a continuous flushing, formation of furrows, deep gullies and ravines. The soil loses power due to the flushing of the upper horizon. The morphology of the soil horizons seen significant cuts seal. Priority pollution elements are lead, copper and zinc. Concentrations of heavy metals exceed maximum permissible concentration. The negative impact of plant emissions on vegetation is manifested by the presence of clumps of sparse vegetation, surviving the individuals willow and dropped copies, lack of vegetation over large areas. The vast majority of plants is in a depressed state. Under the influence of toxic emissions on the leaves are formed burns, there is drying branches and axial crop shoots, weakened vegetative and generative development.

Survival rate used assortment of trees and shrubs in the technogenic contaminated area was 75%. All plants are planted after the growing season are in a weakened and depressed. The protective plantations enterprises industrial zone and pilot plantings, tree crops are subject to considerable damage of toxic gases during the growing season. In particular, the appearance of chlorotic spots and leaf margins desiccation, loss of blossoming buds, young shoots and generative organs. A more satisfactory growth and development rates among industrial zone landings detected in *Syringa* L., *Euonymus europaea* L., *Sorbaria sorbifolia* (L.) A. Br and *Symphoricarpos albus* (L.) Blake., *Spiraea japonica* L.

Despite the short duration of the test (2years) the effects of biochar carbonized rice husk to neutralize toxic compounds and improve the sustainability and survival of plants we can say on the positive effects. To improve the performance needed to identify the necessary dosage of biochar, cultivation depth and duration of influence. Creating a sorption barrier is possible with the integrated application of biochar with the addition of mineral dressing, stimulants, phytoregulators and others. The drug improves the physico-chemical composition of the soil and increase the resistance of plants to stressful environmental conditions.

In experimental plantations, tree crops susceptible to significant damage of toxic gases during the growing season. In particular, the appearance of chlorotic spots and leaf margins desiccation, loss of blossoming buds, young shoots and generative organs. Analytical data is possible to determine the content of heavy metals in the soil as a gross, and their mobile forms. Priority pollution elements are zinc, lead, copper and cadmium. As a result of analysis of the content of heavy metals in the investigated chernozem leached soil on all elements exceed the maximum permissible limits. Increased concentrations of heavy metals observed in the upper layers. With the zinc plant are emissions of heavy metals, which have a negative impact on soil and vegetation area zinc plant. This area is very dirty.

Excess dirt shrub plants growing in this area compared to the control plots, with their growing on shrub plant species is: Cadmium - in 351.56 times; zinc - to 218.09 times; Lead - in 212.41-fold, etc. All plants are planted after the growing season are in a weakened and depressed. In certain instances, there is a tendency to dried out against a background of weak growth and the total weight of the plants, the death of a number of skeletal shoots that have a negative impact on the nature of the over-wintering in subsequent years. (2014-2015). At risk are additionally not less than 9% of the number of planted species.

Despite the short duration of the test (2years) the effects of biochar carbonized rice husk to neutralize toxic compounds and improve the sustainability and survival of plants we can say on the positive effects. To improve the performance needed to identify the necessary dosage of biochar, cultivation depth and duration of influence. Creating a sorption barrier is possible with the integrated application of biochar with the addition of mineral dressing, stimulants, phytoregulators and others. The drug improves the physico-chemical composition of the soil and increase the resistance of plants.

Conclusion

Zinc Plant Emissions of heavy metals pollute the environment, the emission area of distribution in circumference occupies a large area of disturbed soil cover and devoid of vegetation, with the manifestations of erosion processes in the form of failures, gullies, and flushing of the upper layers of the soil. Protective plantation enterprises of the industrial zone and pilot plantings, tree crops are subject to considerable damage of toxic gases in the form of the appearance of chlorotic spots and leaf margins desiccation, loss of blossoming buds, young shoots and generative organs.

The ash composition of man-made landscapes plants shows that different parts of the plants absorb and accumulate certain chemical elements. Timbers have a lower ash content. The composition of the ash depends on the growing conditions of the environment as herbaceous and woody plants. The spectral and electron microscopic analysis of polluted soil showed about biochar sorption element zinc. In spite of the short duration of the test (2years) the effects of biochar carbonized rice husk to neutralize toxic compounds and improve the sustainability and survival of plants can be stated about its positive effect. To improve the performance needed to identify the necessary dosage of biochar, cultivation depth and a long time his stay in the soil.

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