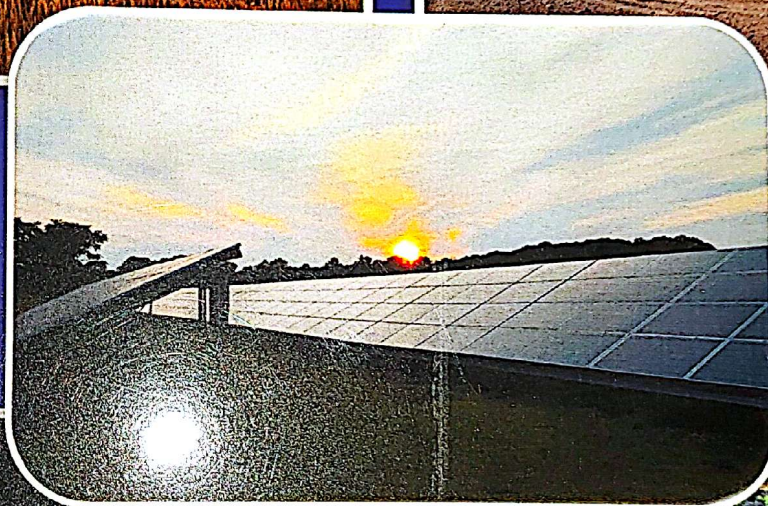
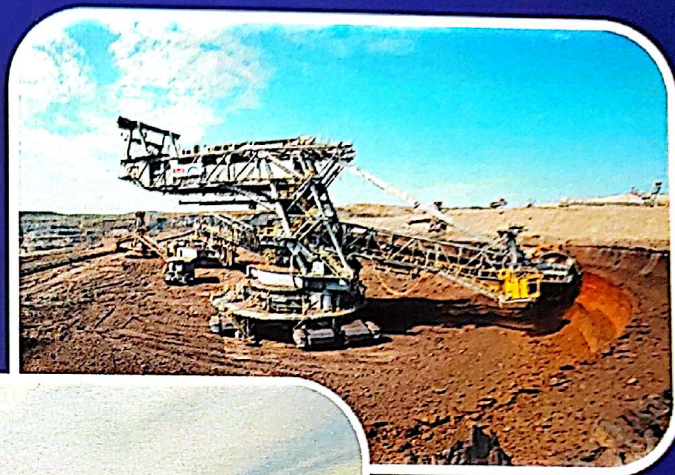


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MINING AND ENVIRONMENTAL PROTECTION**

**MEP 23  
PROCEEDINGS**



**9. Međunarodna konferencija  
RUDARSTVO I ZAŠTITA ŽIVOTNE SREDINE  
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**Sokobanja  
24-27.05.2023.**



9<sup>th</sup> International Conference

**MINING AND ENVIRONMENTAL PROTECTION**

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**MINING AND ENVIRONMENTAL PROTECTION**

**PROCEEDINGS**

Editor  
Prof. dr Ivica Ristović

Sokobanja

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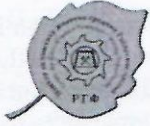
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## **THE APPLICATION OF BIOCHAR ONTO SOILS-BENEFIT FOR OVERALL ENVIRONMENT**

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***Abstract:** Biochar-stable, solid, carbon rich material has gained interest in the last decades as a versatile material for waste reduction whose applications in various fields can increase the efficacy of the circular economy. Biochar has demonstrated possibilities in the field of reducing negative environmental impact of different process, positive effects on climate change and sustainable energy support. All of this is connected to the biochar's intrinsic properties, impacted by certain variables such as feedstock type, pyrolysis conditions, materials modifications etc. Biochar and its application is typical example on how waste resources are upcycled to make a material which can be further used towards environment improvement. It has potential to be used as one of the climate change mitigation options, in agriculture, wastewater treatment, anaerobic digestion and various other sectors. This paper describes some of the possible uses of biochar, with special accent paid on its application onto the soil.*

***Keywords:** biochar, pyrolysis, contaminated soil, agriculture, circular economy*

### **1. INTRODUCTION**

The population growth, continuous non-renewable resources depletion and serious environmental threats caused by industrial growth, induce the necessity of the solutions based on circular (bio)economy which might help in achieving more sustainable future. According to the data from 2019 presented by the Food and Agriculture Organization (FAO), food processing industry is the fastest growing industry sector in the world, where the global demand for food is expected to rise by app. 60% by 2050. Food production generates significant amounts of waste, especially in fruits/vegetables processing industries (FVPI), where biodegradable lignocellulosic waste (LCW) represents app. 25-30% of the raw materials [1]. This biomass includes peels, rind, seeds, core, stones, pods, shell, pomace, etc. In most cases, this type of waste is landfilled, representing unsustainable practice with environmental hazards. Besides rising of greenhouse gases (GHGs), pollutant leachates and chemical as well as biochemical oxygen demand, it exemplifies wasting of food commodities, land, water, fertilizers, chemicals, energy and labor. The reduction of negative impacts of generated LCW might be achieved by applying the concept of a circular economy, which takes primary and secondary LCW from FVPIs and finds their further beneficial purpose.

The complex bio-structure of LCW allows its thermo-chemical conversion into high surface carbon rich material with abundant functional groups, biochar, with multifunctional environment remediation role [2]. Solid biochar has a multi-scale application, ensuring carbon sequestering and reducing GHG emissions at the first place [3]. The application of biochar is a potential avenue for valorization of non-edible waste into environment protection purposes, where the water purification and soil remediation represent one of the main options. According to Shackley et al [4], biochar represents the porous carbonaceous solid material produced by thermochemical conversion of organic materials in an oxygen-depleted atmosphere which has physiochemical properties suitable for the safe and long-term storage of carbon in the environment and, potentially, soil improvement. Biochar is prepared through thermochemical conversion of various biomasses

under limited oxygen conditions at particular temperature, where the effective transformation of chemical composition and physical state of the starting biomass is occurring. In slow pyrolysis, the chemical elements of biomass undergo the process of de-polymerization, decomposition and cross-linking, which results in a carbon-rich material-biochar. Many authors claim that biochar is a possible replacement for activated carbon due to its surface functional groups, porous structure, non-carbonized components and specific surface area [2,5]. Most commonly raw biomasses used for biochar production are marine/aquatic organisms, industrial bio-wastes, and animal manure, forest and agriculture residues [6]. In order to improve biochar physio-chemical properties, functionalization, metal oxide impregnation and surface oxidation processes might be done [7]. Biochar can support local circularity by its application in a variety of processes such as pesticide sorption, water decontamination, immobilization of heavy metals, nutrient retention, soil conditioning and also as a replacement of activated carbon [2]. Thanks to its chemical (pH, C content, hydrophobicity, aromatic carbon structure) and physical (porosity, surface area) properties, biochar is known to lower heavy metal bioavailability, lower Al and Fe toxicity to plant roots and microorganisms, increase plant nutrient availability, act as a liming agent, raise soil pH, improve soil structure, lower nutrient leaching, and improve nutrient use efficiency [7]. Biochar has also found its application in various industry fields such as animal feeding, improvement of anaerobic conditions in bio-refining processes, water depollution, catalysis production, energy source etc. Summarized application of biochar is presented at Figure 1.

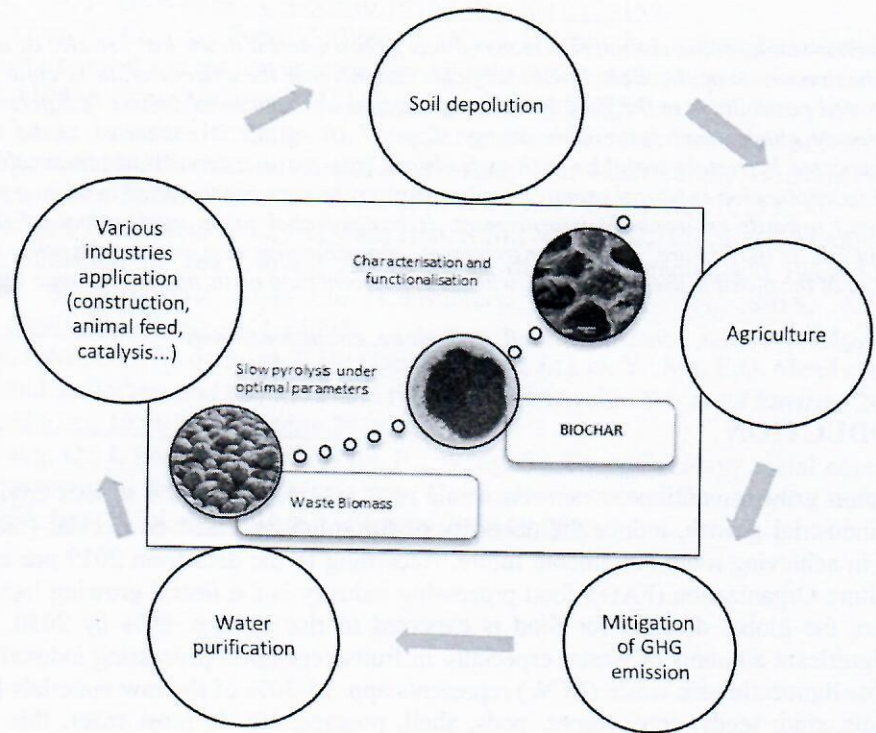


Figure 1. Route of biochar production and its various applications

The application of biochar results in decreasing of the amount of untreated waste on landfills, directly reducing GHG emission, and thereby accomplishing the circular economy based environmental management. The production of biochar from biomass waste serves as one of the most sustainable ways to treat waste because it requires less energy for its conversion compared to other techniques [2].

This paper analyses the application of biochar on the basis of previous studies, with special accent put on the remediation/stabilization of toxic metals present in soil; it also presents benefits of biochar utilization in agriculture, describing positive effects on the crops growth. This might give an opportunity towards developing a stronger CE in Serbia, promoting the use of nutrients present in various waste streams, energy and environment clean-up, as well in agricultural practice.

## 2. SOIL POLLUTION IN SERBIA

Biomass burning and composting are often employed in agricultural practices as waste management methods, thus contributing to nearly 13.5 % of the total anthropogenic emissions of the GHG [8]. The impacts of biochar on soil physicochemical and biological properties is well known; high porosity, large specific area, and alkalinity of biochar can change soil pH value and redox potential (Eh), together with improvement of soil organic matter retention, and the water-holding capacity [8]. In Serbia agricultural land dominates with over 54.7% of the total territory of the country. Forests and semi-natural areas cover almost 39.96% of the country (deciduous forests - 27%), while land classified as artificial areas covers almost 3.69% of the territory, and the remaining approximately 1.65% is classified as wetlands and water basins.

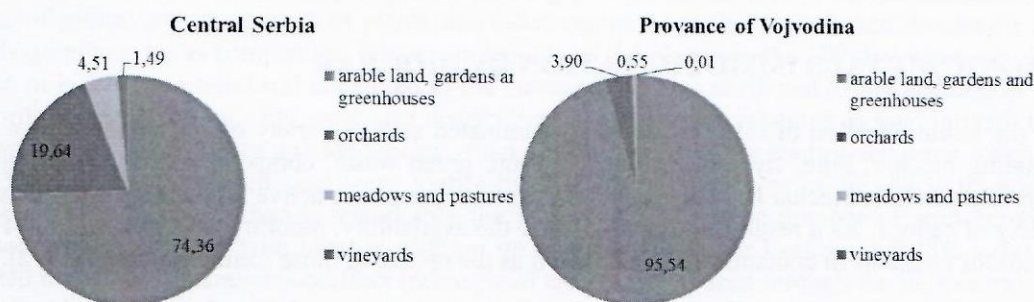


Figure 2. Agricultural land usage (%) in Central Serbia and Province of Vojvodina

Central Serbia is dominated by soils with weakly acidic and acidic reactions, carbonate-free and weakly carbonate, weakly humus to humus, with very low and low easily accessible phosphorus and soil with optimal and high content of easily accessible potassium. The Province of Vojvodina is dominated by weakly alkaline soils, differently provided with carbonates, weakly humus to humus, with different content of easily accessible phosphorus and soils from optimal to high content of easily accessible potassium.

The results of the analysis of easily accessible phosphorus show that the largest number of samples of arable land and gardens, orchards and meadows and pastures are in the class of very low and low content ( $P_{2O_5} < 5$  and 5-10 mg/100g), while vineyards are mostly in the class of low content of accessible phosphorus (5-10 mg/100g). The results of agricultural land fertility in 2019 show that the largest number of samples has a low content of organic carbon content. The measured average content of organic carbon in agricultural land of the Republic of Serbia at a depth of 0-30 cm is 1.87% and belongs to the category of low content.

Pollution situation of agricultural land in Central Serbia and Vojvodina indicates that in individual cases the remediation values of certain parameters were exceeded [9]. The control of fertility and content of dangerous and harmful substances in the lands under plum orchards of the Šumadija area was conducted at more than fifty locations with a total of 106 samples at depths of 0-30 cm and 30-60 cm. The results of the analysis of 53 samples at a depth of 0-30 cm show exceeding the limit value for Cu, Zn, Ni, Co and Hg. The pollution situation of agricultural land in Vojvodina also indicates exceeding values of metals such as Cd, Hg, Ni, Cu and Zn, while remediation values were exceeded for Cu in 17 samples (3.81%) out of a total of 447 tested samples at a depth of 0-30 cm.

In 2018/2019, the degree of endangerment of land from chemical pollution in urban zones in 18 major cities was monitored, and total of 397 samples were examined. The most frequent exceeding of limit values was recorded for Zn, Cu, Ni, Co, Cd, PCB and DDE/DDD/DDT.

The Serbian Environmental Protection Agency [9] report, published in 2020, showed that there are 213 contaminated or potentially contaminated sites. Among the other pollutants, metals such as: Cu, Zn, Ni, Co, Pb, Cd and As are mainly present, often exceeding the maximum acceptance threshold. The area degraded by ore extraction is 195.35 ha, while the area degraded by tailings disposal is 85 ha. Negative impacts of tailings disposal onto environment are widely present and, unfortunately, well known. Mine tailings have a negative impact on water, land and air in his immediate vicinity. For example, mine tailing from Grot mine flotation represents unique source of contamination for the wider area around the source,



inducing releasing of huge amounts of HM [10]. The results presented [10] indicate high concentrations of Zn, Cd and Pb from the tailings and the nameless water, and Pb and Fe from Seliski stream are classified in the third and fourth class. This water cannot be used as drinking water or for irrigation due to high contents of Cu, Zn, Cd, Zn and Pb, posing risk to human health. Lands in the vicinity of tailings are mainly processed and the main source of the soil pollution is the mineralized dust, blown from the tailings. HM are above the limit in the soil, and below the remediation concentration, while the contents of Pb, Zn and Co are in the depressive range. The presences of heavy metals in soil are a constant potential threat to the local agriculture population. In deposition tanks, placed around flotation tailings, soil pollution was found to depend on micro locations of tanks and cumulative time interval. The highest contents of Pb, Zn, Hg and Cd were found in the vicinity of the flotation.

### 3. TOXIC METALS IMMOBILIZATION BY BIOCHAR

For the immobilization of toxic metals in contaminated soils, a variety of amendments have been used, including biochar, lime, fly ash, activated carbon, green waste, compost, and different minerals [11]. Typically alkaline, biochar has large surface areas with numerous active functional groups that can bind a variety of cations. As a result, biochar can lower the availability, mobility, and leachability of potentially hazardous elements in contaminated soil as well as the uptake of those elements by plants [12].

Gong et al., (2022) [13] summarized the most recent studies (until 2021) on biochar's ability to immobilize soil heavy metals (HMs), by both pristine and modified biochar. The two types of HMs that contaminate soil are oxy-anionic HMs (As and Cr) and cationic HMs (Pb, Hg, Cd, Cu, Ni, Zn, etc). Both materials demonstrated different immobilization mechanisms and effects for the immobilization of present pollutants. By modifying biochar with compounds that can precipitate with As, the toxicity of oxy-anionic As can be reduced. Modifying the biochar with reducing materials is the most effective technique to remove of oxy-anionic Cr(VI). Therefore, precipitation and reduction of oxy-anionic HMs by pristine biochar/modified biochar are the main mechanism for reducing HMs toxicity. HMs that are cationic can be successfully immobilized by pristine biochar. While cations are primarily adsorbed by ion exchange, complexation, and precipitation, oxyanions are mainly adsorbed by electrostatic adsorption and redox reactions. Ion exchange, electrostatic interaction, precipitation, physical adsorption, and complexation are some of the mechanisms utilized by biochar to adsorb and immobilize heavy metals in polluted mining soils; these mechanisms can work individually or synergistically [14].

Sachdeva et al., (2023) [15] gathered from more than 200 publications related to the immobilization efficiency of biochar in agricultural soil and its effects on soil from various perspectives. Cationic heavy metals (Pb, Cd, Cu, Ni) and Cr mobilization and uptake by plants were effectively reduced by pristine biochar, while modified biochar successfully reduced As in plant and soil systems. The use of biochar not only successfully immobilized heavy metals in the soil but also increased soil fertility and agricultural productivity.

Based on a literature review, Gao et.al. (2022) [16], observed that in the mining soil remediation field of study, biochar is gaining more and more interest. Factors affecting biochar remediation of contaminated mining soils are: soil properties, biochar properties, application amount, particle size, and combined materials. The main factor affecting how well biochar immobilizes heavy metals in mining soils is the pH of the soil. Biochar enhances the physicochemical characteristics of soil while providing nutrients necessary for plant and microbial growth, by changing the soil's composition and the species of the heavy metals, lowering their bioavailability. In this paper was emphasized that it is necessary to establish standardized procedures for employing biochar to remediate mined soil.

Wang et al., (2021) [17] concluded based on numerous studies that the soil environment has a significant impact on the actual immobilization effect of biochar. The actual immobilization impact of biochar can be considerably influenced by biotic factors like earthworms, microbes, and plant roots as well as abiotic factors including soil pH, redox potential, DOM (Dissolved Organic Matter) content, acid rain, and biochar's physical and chemical characteristics. Several studies confirmed that biochar immobilization is effective over a period of at least 2-3 years, or even 5 years.

#### 4. BIOCHAR as ALTERNATIVE to CHEMICAL FERTILIZERS

The demand for food security is constantly increasing with the world population growth. Although the global food production has benefitted from application of chemical fertilizers, their intensive use has emerged environmental problems, such as hardened soil, decreased soil fertility, polluted soil, water and air and the release of greenhouse gases. An alternative to chemical fertilizers that can be sourced in abundant amounts, promoting global food production, reducing GHG gases and positively affecting soil health and quality, biochar appears as an important promising solution [18].

The effects of biochar on plant growth are very positive. Yadav et al. (2016) [19] have examined influence of biochar (made from *Napier grass*) on the growth of plants in both neutral and acidic soil. In the case of neutral soil, the growth of plants was faster compared to the control even though the number of seeds germinated was comparable. The mean heights of the plants on the 20<sup>th</sup> day were app. 20% for the case of biochar amended soil compared to the control. This was attributed to the addition of biochar which influence the soil porosity, pore-size distribution and soil–water relations as seen through the high water retention capacity of the applied biochar. Also, in comparison to the control, the dried weights of 10 plants from biochar amended pots were higher by 30% (for 0.25% w/w of biochar). In acidic soil, addition of biochar didn't change remarkably the plant heights, but the number of seed germinations increased with an increase with biochar addition up to 57% (at biochar loading of 0.25% w/w). It was attributed to the acid neutralization effect (presence of carbonates as seen through the IR spectra), and the pH of the biochar (11.14) which suggested that biochar addition to the acidic soils provides the much necessary pH elevation that promotes an enabling environment for plant growth. In addition, the dried weights of the plants from the biochar amended pots were higher by 15% than in the control.

Effect of biochar amendment on growth and heavy metal availability to the wheat crop was examined by Pandey et al., (2022) [20], who showed that HM stress hindered the development of wheat plants. The germination rate, shoot length and shoot dry weight of wheat plants were 46.6%, 15.26 cm, and 0.61 g, respectively, under the control set-up. By addition of biochar (3%) made from *Lantana* plants, these values increased by 50.2%, 16.12%, and 90.16% as compared to the control setups. This was attributed to boosting the synthesis of chlorophyll content and improves photochemical reactions and photosynthesis efficacy in leaves when biochar was applied in crop fields. Also, they assumed that biochar addition in soils promotes plant roots to grow deeper into the soil, making water and nutrients adsorption easier. The same authors also analyzed the content of heavy metals in wheat crops harvested from control and biochar amended soils. After 120 days, the accumulated concentrations of Cr, Cd, Cu, Pb, Ni, Zn, Mg, and Fe in the harvested plant shoots from the control set-up were 27.57, 0.62, 22.25, 0.89, 3.03, 21.55, 143.67, and 234 mg kg, respectively. These values drastically decreased after application of two types of biochars, as can be seen from Figure 3.

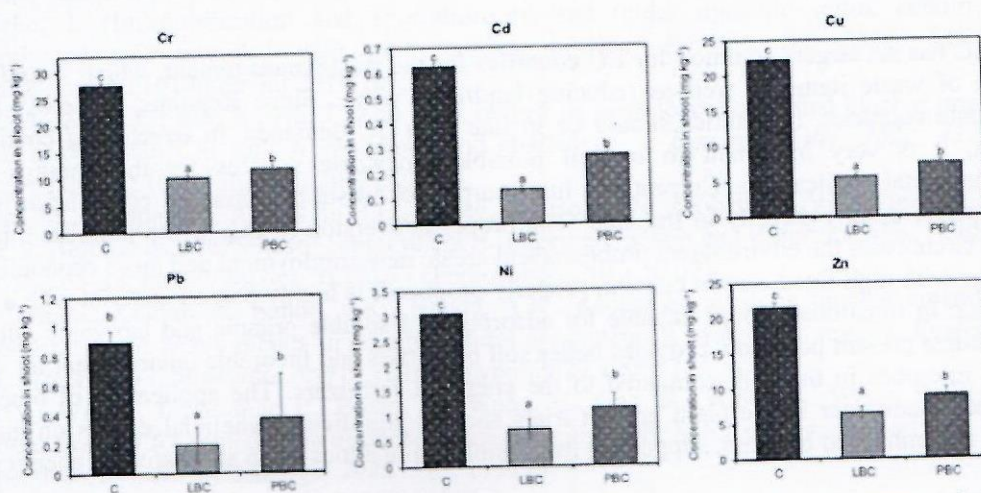


Figure 3. Heavy metal concentration in wheat plant biomass harvested from control and different setups of biochar [20]

The application of biochar onto the soil greatly increased the soil and plant enzymatic activities, by the improvement of nutrients level, porosity, moisture contents, carbon supply, etc., which significantly affected the microbial processes in the soil ecosystem. This could be linked to a reduction in the availability during the stabilization process, which helps to alleviate microbial metabolic restrictions [22]. Khan et al. (2020) found that adding biochar to soil contaminated by lead, increased the enzyme profiles [22]. The decrease in lead toxicity to associated microbial species could be due to the immobilization of metals by biochar and its assisted chemical transformations into insoluble forms. Biochar also affects the diversity and composition of the soil microbial communities, contributing to soil microbial interactions and adjusting the soil nutrient cycle [23]. The microbes get attached to the biochar micro pores by hydrophobic attraction, electrostatic forces, and become more resistant to leaching [24]. Simultaneously, presence of the microbes on biochar surface significantly increases microbial biomass carbon in soil compared with chemical fertilizers. Some studies showed that a change in microbial community structure and an increase in microbial action due to biochar application has heightened the N and P retention in the soil [25].

Zhang et al., (2023) showed that under normal storage conditions, biochar is prone to colonization by a large number of beneficial microorganisms (*g. Streptomyces*, *g. Pseudonocardia*, *g. Amycolatopsis*) from the storage environment and the amount of colonization increased when such biochar is applied to the soil [26]. The authors believe that after biochar application to the soil, the relative abundance of microorganisms that colonized the surface of biochar changed due to differences in the soil environment but the basic composition of the microbial community remained almost constant. Zhai et al., (2023), who studied the response of N<sub>2</sub>O related microorganisms to addition of biochar into chicken manure compost, discovered the alteration of the compost microenvironment due to change in the structure of the N<sub>2</sub>O related bacterial community [27]. They have noticed that *Ornithinibacillus* became the dominant microorganism playing a regulatory role in the nitrification process, by denitrification inhibition and thus reducing N<sub>2</sub>O emissions. Wang et al., (2023) studied long-term effects of biochar retention on the soil nitrogen supply capacity of bulk and rhizosphere soil in brown earth, showing that the elevated application rates significantly enhanced soil organic matter, and total nitrogen, and improved pH in both bulk and rhizosphere soils [28].

However, some studies reveal that biochar overuse can jeopardize microorganisms due to its potential to absorb toxins, such as HMs and pesticides, and then to release them from the biochar surfaces [29]. According to Nguyen et al., (2016) biochar also may result in a decrease in bioavailability and mobility of many organic pollutants [30]. All those findings confirm that some of these issues have to be studied in more detail and to reveal the positive or negative effects depend on the biochar characteristics and to soil types.

## 5. CONCLUSION

The EC has set targets common for EU countries for the waste management, which include measures to re-use of waste items as well as reducing landfilled waste. Since Republic of Serbia is one of the candidate countries, its politics should be in line with EU demands. In developing countries, such as Serbia, it is very important to use all possible renewable sources for the energy, material and environmental applications. Currently, a huge surplus of waste biomass, are either landfilled or burned improperly, usually directly in the land. The proper conversion of this waste biomass into the biochar might circumvent the environment problems and create new employment and more economic advantages. Biochar with high fixed carbon content, properly produced, is highly porous material with a large surface area rich in functional groups capable for adsorption of soluble organic and inorganic nutrients, which immobilize present pollution, provides better soil properties and favorable environment for the growth of useful microbes in the soil, compared to the chemical fertilizers. The application of biochar as a soil amendment/conditioner in the plant growth trials showed significant beneficial effects on increased plant height and enhanced biomass, supporting its possible applications as an alternative to chemical fertilizers.

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