Research Progress of Environmental Risk Substances in the Preparation of Biochar

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Abstract. Biochar is a kind of solid material containing high carbon, which is obtained from biomass such as agricultural and forestry wastes through photosynthesis in oxygen free or low oxygen environment and pyrolysis at high temperature. It has many advantages, such as wide source of raw materials, high specific surface area, developed pores, and high stability. With the wide application and promotion of biochar in various fields, some hazardous substances to the environment generated in its preparation process, such as heavy metals and metalloids, polycyclic aromatic hydrocarbons, persistent free radicals, soluble organics and metal cyanide, should also be focused on and studied. In this paper, three types of environmental risk substances (i.e. heavy metals, polycyclic aromatic hydrocarbons and persistent free radicals) are studied, and their harm to the environment and ecological are explored, as well as the prospects for future development. Through careful selection of raw materials and the optimization of preparation conditions, the toxicity and harm can be suppressed to some extent.

Keywords: Biochar, environmental risk substances, heavy metals, polycyclic aromatic hydrocarbons, environmental persistent free radicals.

1. Introduction

Biochar is a kind of solid material with high carbon content, which has a large number of microporous structures. Its application in the field of environmental remediation can not only adsorb heavy metals in soil, promote plant growth, but also absorb a lot of greenhouse gases. The preparation process of biochar is generated by high-temperature pyrolysis of organic waste or biomass. However, some environmental risk substances, such as heavy metals, polycyclic aromatic hydrocarbons and environmental persistent free radicals, will inevitably be generated during the preparation process, so this essay will focus on the generation and harm of these risk substances [1].

2. Heavy Metals

2.1. Heavy metals carried in the preparation of biochar

Heavy metals refer to metals with a density of more than 4.5g/cm^3. In the aspect of environmental pollution, heavy metals primarily refer to heavy elements with significant biological toxicity, such as mercury, chromium and metalloid arsenic [2]. These heavy metals cannot be degraded, so it is a very important treatment method to adsorb heavy metals through biochar. However, heavy metals may exist in the raw materials biochar. Theoretically, various crops including corn, rice and wheat straw, livestock wastes including pig manure, cow manure and other animal manure organic solid wastes, and even urban sludge can form the feedstock to biochar. When pollutants in raw materials, especially heavy metals that are difficult to volatilize, they can be concentrated in biochar, thus becoming a potential risk of environmental pollution. During the preparation of biochar, these pollutants will accumulate in biochar. If these raw materials, such as organic waste (such as sewage sludge), are used to produce biochar, they will often contain a large amount of heavy metals and increase the content of heavy metals in the environment.

Stefaniuk et al. compared the biochar prepared from the sludge of three biogas plants and found that the pyrolysis temperature and the type of heavy metals are the key factors affecting the content of heavy metals in the biochar. When the pyrolysis temperature rises from 400℃ to 800℃, the content of Cr, Cu, Cd, Pb and Mn in the biochar increases with the increase of the pyrolysis temperature, while the content of Zn and Ni increases first and then decreases [3]. This is because during the high-temperature pyrolysis process, the loss of a large amount of organic matter leads to the concentration of heavy metals in the biochar. Therefore, the concentration of non-volatile metals (such as Fe, Cu, etc.) will continue to increase with the increase of the pyrolysis temperature. Some volatile heavy metals, such as Cd, Pb, Zn, are easy to volatilize at high temperatures, so their concentrations will increase first and then decrease with the increase of pyrolysis temperature. Moreover, since the biochar contains a large number of mineral element oxides, carbonates, phosphates and other substances, its pH is generally higher than 7. With the increase of pyrolysis temperature, the pH of the biochar will gradually increase, and the heavy metals in the biochar will also change from the binding form with low stability to the binding form with high stability.

In a study, it was found that with the application of biochar, the content of copper and arsenic increased by more than 30 times, and the C and pH in soil also increased [4]. Moreover, the organic elements of biochar with high carboxyl content would stimulate copper in alkaline soil. Similarly, the application of biochar can increase the mobility of copper and arsenic, but the effect on cadmium is not obvious. These heavy metals have become toxic pollutants in soil due to their bioaccumulation potential for microorganisms and macroorganisms. These pollutants may cause continuous harm to the environment and affect the health of plants, animals and human beings.

2.2. Impact of heavy metals on the environment

In general, heavy metals are the first to harm soil microorganisms, and the number of microorganisms that do not adapt to heavy metals will be drastically reduced or even extinct.

The presence of Mn will enhance the adsorption capacity of biochar on metal As, which is conducive to the removal of As from contaminated soil. However, as a heavy metal, excessive Mn content will also pollute the environment and endanger the health of animals and plants; Metallic Ni is one of the essential micronutrients of some lower organisms and plants. It is widely distributed in nature, but it is also a carcinogenic toxic element. It can be accumulated in various human organs and has carcinogenic mutagenicity. Heavy metals are enriched in plants through the food chain. Studies show that with the increase of cadmium pollution in surface soil, cadmium content in rice grains gradually increases. When cadmium mass fraction in upper soil reaches 5 mg/kg, cadmium mass fraction in rice grains reaches 0.264 ~ 0.337 mg/kg, and cadmium mass fraction in upper soil reaches 10 mg/kg, Cadmium in grain can be as high as 0.418 ~ 0.554 mg/kg.

Secondly, heavy metals can damage some tissues and functions of plants, thus reducing the yield and quality of plants. For example, redundant cadmium content in the soil will destroy the chlorophyll structure of plant leaves and eventually lead to the decline of plants. When the copper and zinc content in the soil exceeds a certain limit, the roots of crops will be seriously damaged, affecting the absorption of water and nutrients by plants, resulting in poor growth and even death. It is estimated that 70% of the heavy metal cadmium in the human body comes from vegetables in food. The cadmium accumulated in vegetable crops mainly comes from garden soil, and part of it comes from irrigation water. In addition, heavy metals in soil can be transferred into surface water system through rainwater leaching and surface runoff, and then pollute underground water through the interaction between surface water and groundwater, posing a threat to drinking water safety [5].

Moreover, heavy metals are highly toxic and difficult to be degraded. After entering the water body, they can directly act on the human body through drinking water or domestic water, and can also be enriched and absorbed by aquatic animals and plants, entering the food chain and endangering human and animal safety. Scientific workers' experiments have proved that the solution with the mass concentration of cadmium of 1.0 mg/L can poison the palisade algae for 24 hours, which is characterized by shrinking of the cytoplasm and destruction of the chloroplast. Heavy metals also have a strong toxic effect on aquatic animals. Short exposure of fish to high concentration of heavy metal solution will lead to stress reaction, and the immune capacity of fish will be reduced. The accumulation of heavy metals such as copper, zinc and manganese has certain effects on the sex and body length of fish.

The Cf, Er and RI of sludge and its biochar determine the risk level of heavy metals. The Cf of Cd and Cr in air dried sludge (DS) are 1.04 and 1.74 respectively, which are the main risk factors. The Cf of Pb is less than 1, so there is no risk. The ecological risk of Cd increases to 1.54 (maximum) with the increase of cracking temperature between 300℃ and 700℃, decreases after 700℃, and decreases to 1.45 at 900 ℃, which is a low ecological risk; With the increase of cracking temperature, the risk of Cr first decreases and then increases to 2.86 at the maximum, and then the fluctuation decreases to the minimum, 0.31. There is no risk.

3. Polycyclic aromatic hydrocarbons (PAHs)

3.1. PAHs generated during the preparation of biochar

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants that can cause cancer, teratogenesis and mutagenesis. They refer to aromatic hydrocarbons containing two or more benzene rings. They are mainly composed of two ways: one is non condensed ring type, including biphenyl and biphenyl and polyphenyl aliphatic hydrocarbon; The other is the fused ring type, that is, two benzene rings share two carbon atoms.

A small amount of research has found that if the biochar is prepared with tall fescue, pine, cow dung, rapeseed cake, straw and sludge as precursor materials, a certain amount of polycyclic aromatic hydrocarbons will exist in the biochar, and a certain amount of PAHs will also be detected in the gas and bio oil generated when the material is decomposed by heating. In addition, PAHs in the preparation and use of biochar may cause secondary pollution to the environment, which requires special attention. In addition, other studies have found that the pyrolysis temperature has a very significant impact on it. For example, with the increase of the pyrolysis temperature at 250~600℃, the content of PAHs in crop residues such as straw biochar will decrease; However, the PAHs content of sludge based biochar increases with the increase of pyrolysis temperature at 500~700℃ [6].

At present, there are two main ways to generate PAHs in the process of preparing biochar: first, when the pyrolysis temperature is below 500℃, some single molecules generated by biomass pyrolysis form ring structures containing heteroatoms, dehydrogenation, dealkylation from hydrocarbon molecules and other reactions, or lignocellulose polymers and lipids generate PAHs through aromatization reaction; The second is that when the pyrolysis temperature is above 500 ℃, polycyclic aromatic hydrocarbons are formed through free radical pathway, and larger aromatic structures are generated through high temperature.

Phenanthrene(NAP) is a condensed aromatic hydrocarbon containing three benzene rings and naphthalene(PHE)is the simplest condensed aromatic hydrocarbon, which is consisted of two benzene rings sharing two close carbon atoms. NAP and PHE (both accounting for more than 50%) are the main components of PAHs in macroalgae based biochar. Research results show that NAP and PHE contribute the most to the total amount of 16 PAHs in biochar.

However, BaP of Class I carcinogen was only detected in a small amount (0.46%~1.34%) of Sargassum fusiforme biochar prepared at 500 °C, Sargassum biochar, centipede biochar, and water shield biochar prepared at 400 ° C, and DahA, which is listed as Class 2A carcinogen by IARC, were not detected in any large seaweed biochar. Therefore, it can be further speculated that the potential risk of 16 PAHs in large seaweed based biochar is low [7].

3.2. Environmental hazards of PAHs

PAHs are the environmental carcinogens that were first discovered, studied most and distributed most widely, with the largest total number and the highest frequency of contact with human bodies. PAHs can accumulate in the environment, pollute water, air and soil, and then enter the food chain. At present, more than 400 kinds of carcinogenic PAHs and their derivatives have been found, and hundreds of thousands of tons of polycyclic aromatic hydrocarbons are discharged into the atmosphere every year.

Among polycyclic aromatic hydrocarbons, benzopyrene has the greatest impact on the human body. It is a carcinogen and fat soluble substance. When inhaled into the body, lungs or blood, it will lead to lung cancer and cardiovascular disease.

In the past 30 years, China's industry has developed rapidly, the urbanization process has been accelerated, and the number of motor vehicles has increased significantly, leading to the increasing pollution of PAHs, which seriously threatens the ecological environment and the safety of organisms. With the rapid economic growth, the output of aquatic products in China has ranked first in the world for more than 20 consecutive years. Fish is delicious and nutritious, which is popular among people. The PAHs in water can easily enter the fish body, thus becoming one of the sources of human intake of polycyclic aromatic hydrocarbons. In addition, pollutants will enter the body of workers engaged in production and transportation of biochar through respiratory inhalation, skin contact and dietary exposure, which may increase the incidence rate of cancer.

4. Persistent free radicals (PFRs)

4.1. Formation of environmental persistent free radicals

Free radicals refer to molecules, ions or groups containing unpaired single electrons formed by the homogeneous cleavage of covalent bonds of compound molecules under the influence of light, heat, radiation and other external conditions.

Persistent free radicals are formed when organic components of biomass are pyrolyzed on the surface of environmental media such as metal oxides. These molecules are considered as precursors to the formation of persistent free radicals. Precursors of environmental persistent free radicals include dioxins, chlorinated aromatic hydrocarbons, aromatic compounds, lignin, chlorogenic acid, quinones, etc. Due to the pyrolysis of biochar in the preparation process, it is inevitable to produce environmental persistent free radicals, and different biochar will also form different environmental persistent free radicals.

The formation of biochar PFRs is closely related to some specific organic substances, such as phenols, chlorobenzene, chlorophenols, and transition metal oxides, such as ZnO, CuO, NiO, etc. These organic molecules attach to the surface of the transition metal oxide particles through the chemical adsorption process. The electrons on the organic molecular groups are transferred to the transition metal atoms, where the organic molecules are oxidized as electron donors to form PFRs, and the transition metals are reduced as electron acceptors. The generation of EPFRs is affected by many factors, and the generation of environmental persistent radicals can be summarized as the following process: driven by external energy (heating, ultraviolet radiation, microwave radiation), covalent bonds of biomass macromolecules are split to form small molecular radicals [8].

The main components of biomass are hemicellulose, cellulose and lignin. The temperature of hemicellulose and cellulose decomposition is relatively low (about 200℃), while the temperature of lignin decomposition is relatively high (>300℃). Generally, the temperature of pyrolysis biomass is above 300℃, and hemicellulose and cellulose are basically decomposed into small molecular monomers through polymer depolymerization and other reaction processes. Therefore, the process of biochar formation in biomass pyrolysis products is basically related to the decomposition process of lignin [9].

4.2. Characteristics of EPFRs

There are three typical characteristics of EPFRs, i.e., reactivity, mobility and persistence. Reactivity means that under certain conditions EPFRs can produce reactive secondary free radicals and react with the surrounding environment. Mobility refers that they can migrate with the medium. Persistence suggests that the half-life of EPFRs in the environment can be up to 30 days, so there is more potential for harm.

4.3. Harms of persistent free radicals

The research shows that the biochar rich in EPFRs will induce the production of hydroxyl radicals after entering the aqueous phase, which has a significant retarding effect on seed germination and rhizome growth, and has caused damage to the cell membrane.

Some fused ring substances such as PAHs will form PFRs in the process of molecular structure decomposition and transformation, and these PFRs may be the key factors leading to the formation of dioxins.

It has been reported that biochar PFRs can be used as electron donors to stimulate and activate O_2, H_2O_2, persulfate and other living oxygen ROS, so as to achieve the goal of effective degradation of organic pollutants.

PFRs also do harm to human body. (1) They can reduce the resistance of cells, making the body vulnerable to bacteria and germs; (2) produce chemicals that can violate cells and form carcinogens; (3) It interferes with the normal development of cells, disturbs with their repair function, and makes the cell renewal rate lower than the atrophy rate; (4) They destroy the genetic gene (DNA) tissue in the body, disrupt the operation and regeneration function of cells, cause gene mutation, and develop into cancer; (5) destroy mitochondria (energy storage body) in cells, causing oxidative fatigue; (6) destroy the cell membrane, affect the cell metabolism, and make the cell membrane lose the function of protecting cells; (7) The amino acids needed to invade cell tissues and hormones will affect the operation of the system in the body, leading to a vicious circle and more free radicals. This chain reaction will lead to the harm of free radicals all over the body; (8) destroy proteins and enzymes in vivo, causing inflammation and aging symptoms ;(9) destroy fat, cause lipid peroxidation, and cause cardiovascular and cerebrovascular diseases and other diseases [10].

The immediate addition of biochar to soil is considered to be a method to slow down climate change and restore soil. However, such a large scale of charcoal production also requires a large amount of soil to produce enough biomass. At present, fast-growing forests and other raw materials, which are only planted by the paper industry and agricultural fuel industry, have had a huge impact on the ecological environment and exacerbated climate change. The huge demand for biochar will greatly aggravate these environmental problems, because the use of biochar requires more land to produce charcoal and energy [11].

5. Conclusion

The pollutants in biochar, including endogenous and exogenous pollutants, are the principal consideration influencing the poisonousness of biochar. Therefore, it is a hot scientific issue in the future to systematically study the relationship between pollutant concentration changes and their ecological and health impacts during the aging process of newly prepared biochar, and whether there are certain differences in the harm and impact of biochar on different ecosystems such as soil ecosystem and aquatic ecosystem. Therefore, only by clarifying the application impact mechanism of biochar on different ecosystems can researchers choose different suitable use environments to achieve safe and effective use of biochar.

References

[1] Biochar. https://en.wikipedia.org/wiki/Biochar.

[2] Gholizadeh M, Hu X. Removal of heavy metals from soil with biochar composite: A critical review of the mechanism [J]. Journal of Environmental Chemical Engineering, 2021, 9 (5): 105830.

[3] Miao Shichao, Wu Wei, Fu Yu, et al. Influence of pyrolysis temperature on characteristics of heavy metals in biochar derived from Ulva prolifera [J]. Environmental Science & Technology, 2019, 42 (12): 163 - 167.

[4] L. Beesley, E. Moreno-Jiménez, and J. L. Gomez-Eyles, “Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil,” Environmental Pollution, vol. 158, no. 6, pp. 2282 – 2287, 2010.

[5] Harm of environmental heavy metal pollution. https://mhuanbao.bjx.com.cn/mnews/20161101/785179.shtml.

[6] S. Kloss, F. Zehetner, A. Dellantonio et al., “Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties,” Journal of Environment Quality, vol. 41, no. 4, pp. 990 – 1000, 2012.

[7] Wang Qilu, Fu Yu, Chen Qifeng, et al. Distribution characteristics and toxicity evaluation of polycyclic aromatic hydrocarbons in macroalgal biochars [J]. Transactions of the Chinese Society of Agricultural Engineering (Transactions of the CSAE), 2022, 38 (15): 269 - 276. (In Chinese with English abstract) doi: 10.11975/j.issn.1002-6819.2022.15.029.

[8] Jia H, Zhao s, Shi Y, et al. Transformation of polycyclic aromatic hydrocarbons and formation of environmentally persistent free radicals on modified montmorillonite ite: The role of surface metal ions and polycyclic aromatic hydrocarbon molecular properties. Environ Sci Technol, 201852: 5725 - 5733.

[9] Qin Y X, Li GY, An T C, etal. Advances in ecological and health risks of biochar during environmental applications (in Chinese). Chin Sci Bull, 2021, 66: 5 - 20.

[10] What are the hazards of free radicals? https://m.antpedia.com/news/2862450.html

[11] International organizations against the threat of "biochar" to the environment. http://goootech.com/topics/72010281/detail-10148211.html.