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Investigating the Adsorption Effect of Biochar on Microplastic Pollutants in Soil

Jingyi Sang[1,*], Qianyue Zeng[2]

[1]College of Environment, Nanjing Normal University Nanjing, Jiangsu Province, 210023, China
[2]College of Agriculture, Hunan Agricultural University, Changsha, Hunan Province, 4101258, China
*Corresponding author:26220326@nnu.edu.cn

Abstract:

Microplastic pollution poses a serious threat to soil health and ecological security. Biochar, with its high specific surface area and abundant surface functional groups, shows potential application value in the treatment of soil microplastic pollution. Starting from the physical and chemical properties of biochar, this paper aims to explore the adsorption mechanism of biochar on microplastics in soil and analyze the influence of environmental conditions on adsorption efficiency. Research shows that biochar effectively removes microplastics from soil through physical and chemical adsorption mechanisms. The high specific surface area and abundant surface functional groups of biochar are the key factors for its efficient adsorption of microplastics. In addition, environmental conditions such as pH and ionic strength significantly affect adsorption efficiency, and biochar has a better adsorption effect on microplastics under acidic conditions. This paper points out the intrinsic mechanism of biochar adsorbing microplastics, which is of certain significance for promoting soil ecological security and sustainable development.

Keywords: Biochar, microplastics, soil pollution, adsorption mechanism, pore structure

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1. Introduction

Microplastics are defined as plastic particles and fragments with a size less than 5 mm [1]. As a new type of environmental pollutant, they have been widely distributed in global soil ecosystems. Their sources include degradation of agricultural mulch films, sludge fertilization, atmospheric deposition [2], and wastewater irrigation [3]. It is estimated that the amount of microplastics input into global farmlands through sludge annually is as high as several million tons, and the microplastic pollution caused by the residue of mulch films is particularly prominent in intensive agricultural areas. Microplastics can remain in the soil for hundreds of years and can alter soil structure, inhibit microbial activity, adsorb and release toxic substances such as heavy metals and organic pollutants, threatening crop growth, soil health, and food chain safety. Moreover, microplastics can further break down into nanoplastics, penetrating biological barriers and triggering more complex ecological toxic effects. However, current remediation

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technologies for soil microplastic pollution are still in the exploration stage, and efficient, economical, and environmentally friendly solutions are urgently needed [4].

Biochar is a porous carbonaceous material formed by the pyrolysis of biomass such as straw, wood chips, and livestock manure under limited oxygen conditions. It has a high specific surface area, abundant surface functional groups, and a stable aromatic structure, endowing it with excellent adsorption capabilities [5]. Li Jianrui et al. [6] demonstrated that biochar has an efficient fixation effect on heavy metals such as lead and cadmium. The mechanism involves pore interception, electrostatic attraction, hydrophobicity, and surface complexation. Zhang Yu et al.[7] found that biochar can effectively address the challenges encountered in crop production and regulate soil properties. Under the combined effect of its own properties and the environment, biochar can become an important material for adsorbing microplastics. In recent years, research on the adsorption of microplastics in water environments by biochar has gradually emerged, but its application potential in complex soil media has not been fully exploited.

This article aims to understand the mechanism and adsorption behavior of biochar in adsorbing microplastics, explore which factors affect its efficiency, and reveal its potential application in soil pollution control. Through the analysis of the physical and chemical properties of biochar, this article clarifies the synergistic mechanism of physical adsorption and chemical adsorption, discusses the regulatory effects of environmental conditions and biochar modification strategies on adsorption efficiency, and, in combination with the current situation of microplastic pollution, summarizes the possible future research directions of biochar in the treatment of soil microplastic pollution.

2. Overview of Microplastic Pollution

Plastic refers to plastic particles, fibers, or fragments with a diameter or length of less than 5 millimeters. Based on their sources, they can be classified as primary microplastics and secondary microplastics. Primary microplastics are plastic products that are directly produced as tiny particles, such as microbeads in personal care products like cosmetics and toothpaste, and industrial raw material particles like plastic resins. Secondary microplastics are formed by large plastic waste such as plastic bags, fishing nets, and tires, which gradually break down through processes such as physical wear, photo-oxidation, or biodegradation.

In recent years, researchers have further defined plastic particles with a diameter of less than 1 μm as nano-plastics, as they can more easily penetrate biological barriers and have higher potential toxicity.

Primary microplastics mainly come from industrial products and human releases: such as microbeads in cosmetics (like exfoliating creams and toothpaste) in industrial products, industrial raw material particles (like plastic resin particles), and fibers in synthetic textiles (like nylon and polyester fibers).

As well as particles generated from the wear of automotive tires (accounting for 28% of global microplastic emissions) and peeling off of road marking paints, which are important sources of microplastics in urban atmospheres.

Secondary microplastics mainly come from the degradation of plastic waste and urban activities. For example, the fragmentation of agricultural plastic films is the main source of microplastics in farmland soil. In urban activities, the storage sites of urban solid waste accumulate plastic waste and are compressed, releasing microplastics into the air, becoming potential pollution sources.

The combined effect of microplastics and other pollutants on ecosystems has complex synergistic or antagonistic effects [8-9]. For instance, when polyethylene microplastics are exposed together with high concentrations of salt, they can alleviate the lethal effect of salinization on earthworms, but they will inhibit their growth rate and significantly alter the structure of the intestinal microbial community. At the same time, the combined action of microplastics and acid rain can enhance the adsorption of cadmium, and reduce the accumulation of cadmium in rice seedlings, but the changes in antioxidant enzyme activity and gene expression pathways indicate the existence of toxic interaction. Moreover, the dissolved organic matter released by biodegradable microplastics during photodegradation is more easily utilized by microorganisms, which may accelerate the carbon cycle and pose unknown ecological risks.

3. Introduction to the Advantages and Mechanisms of Biochar in Adsorbing Microplastics

3.1 The advantages of biochar in adsorbing microplastics

Biochar can reduce the bioavailability of microplastics, promote their degradation, and inhibit methane emissions. It has many advantages. For instance, Sun et al. [10] demonstrated that microplastics have toxic effects on plant roots, and due to their physical and chemical properties, they are prone to form combined effects with heavy metals and organic pollutants, thereby exerting higher toxicity on plants. Reasonable application of biochar for adsorbing microplastics can reduce their bioavailability, thereby alleviating the direct toxicity to plant roots [11]. Moreover, the role of biochar in the treatment of microplastic pollution is not limited to direct adsorption; it also achieves comprehensive ecological benefits by regulating soil microbial communities, enhancing nutrient cycling, and carbon sequestration.

The currently known remediation technologies for soil microplastic pollution mainly include microbial and enzyme degradation techniques, as well as biochar adsorption of microplastics [11]. Studies have shown that, compared with the former two methods, biochar, under the presence of microplastics, can more effectively improve soil activity and inhibit methane emissions [12]. In addition, biochar can also effectively enhance the activity of microorganisms and enzymes in the soil, further promoting the absorption and degradation of soil microplastics [11, 13].

On the other hand, the characteristic that biochar is mainly produced from agricultural waste can also effectively utilize organic waste, achieving the goal of “treating pollution with waste”, and better achieving the dual objectives of environmental restoration and resource reuse.

3.2 The mechanism of biochar in adsorbing microplastics

Generally speaking, biochar is mainly made from various types of waste biomass generated by agricultural activities, such as corn stalks, sugarcane bagasse, tree bark, etc. The biomass undergoes incomplete combustion under limited oxygen conditions through different thermochemical conversion technologies, thereby being transformed into biochar. Biochar has a high specific surface area, stable aromatic structure, and a large number of surface functional groups. These characteristics demonstrate its considerable potential in the direction of microplastic adsorption.

The adsorption of microplastics by biochar is mainly driven by surface adsorption, and it may also interact with other factors. Surface adsorption can be divided into physical adsorption and chemical binding. Among them, physical adsorption plays a dominant role. The physical adsorption mechanism of biochar mainly involves pore trapping and van der Waals forces. The pore-trapping mechanism between biochar and microplastics is mainly achieved through the multi-level pore structure and surface shape of biochar to capture microplastics. When microplastics pass through the pores, they are trapped by it. The van der Waals force mainly generates attraction due to the instantaneous dipole induction between molecules on the surface of biochar and those on microplastics. Physical adsorption can quickly capture microplastic particles because they act directly on the surface of biochar. The adsorption process usually reaches equilibrium within minutes to several hours. It is relatively independent of environmental conditions such as pH, temperature, and ionic strength, and can partially restore the adsorption capacity through physical means to reduce the cost. However, the adsorption stability produced by physical action is poor. It is prone to the desorption of microplastics due to water flow erosion or temperature changes. At the same time, it requires a high matching degree for the size of microplastics and has a relatively limited adsorption capacity.

The chemical adsorption mechanism of biochar mainly occurs through the interaction between biochar and the functional groups on the surface of microplastics. The functional groups of both substances form hydrogen bonds and π-π bonds with each other, or generate hydrophobic and electrostatic interactions. The oxygen-containing functional groups on the surface of both substances mainly form hydrogen bonds, while the aromatic ring structure of the graphitized carbon layer can combine with the benzene ring-containing microplastics through π-π stacking. Due to its large number of surface functional groups and low polarity, biochar usually exhibits strong hydrophobicity. Most microplastics themselves also have strong hydrophobic surfaces, making it difficult for them to combine with water molecules in the soil, thus tending to combine with the hydrophobic surface of the same biochar. The advantage of chemical adsorption lies in the fact that it can make adsorption more stable, less prone to desorption, and is also effective for nanoparticles of microplastics that are difficult to retain by physical adsorption. However, it is also more limited by environmental conditions such as pH and ionic strength, requiring more precise regulation. Moreover, the modified materials used in enhancing chemical bonding are prone to cause secondary pollution to the environment.

4. The key factors affecting the adsorption efficiency

The adsorption efficiency of biochar for microplastics is co-regulated by multiple factors, mainly including three categories: material properties, microplastic characteristics, and environmental conditions.

According to the classification criteria of the International Union of Pure and Applied Chemistry (IUPAC), the pores of biochar can be classified into three types based on the size of the voids: macropores, mesopores, and micropores. Macropores refer to voids with a pore size greater than 50nm, mainly adsorbing fibrous or fragment microplastics, but having a low adsorption efficiency for nanoscale microplastics smaller than 1μm[14]. The pore size of mesopores ranges from 2 to 50 nm, making them suitable for adsorbing microplastics with medium particle sizes and enhancing physical interlacing through surface roughness. The pore size of the micropores is less than 2 nm: It has an efficient retention capacity for nanoscale microplastics, but the adsorption capacity may decrease due to pore blockage. Meanwhile, biochar with high pore connectivity can increase adsorption sites. For instance, a three-dimensional honeycomb structure is more conducive to the diffusion of microplastics than a layered structure.

The specific surface area directly affects the density of effective adsorption sites. The larger the specific surface area, the more adsorption sites there are. The research found that the specific surface area of wheat straw biochar increased from 2.31 m^2/g with a particle size of 0.85 mm to 216 m^2/g with a particle size of 0.11 mm, and the adsorption capacity for phenanthocyanins was significantly enhanced [15]. Furthermore, high-temperature pyrolysis (such as 750℃) can significantly increase the specific surface area of bagasse biochar to 540.36 m^2/g, thereby enhancing the adsorption capacity [14].

The oxygen-containing functional groups in the surface functional groups of biochar adsorb microplastics through hydrogen bonds and electrostatic interaction. For instance, due to the higher content of hydroxyl and carboxyl groups on their surfaces, sludge charcoal and paulownia bark charcoal have significantly better adsorption capacities for PET than straw charcoal [15]. The hydrophobic effect of hydrophobic groups such as aromatic rings and alkyl chains dominates the adsorption of hydrophobic microplastics (such as PE). Biochar with a high degree of graphitization can increase the adsorption capacity of PE by 60%, while modified functional groups, such as metal loading or acid oxidation modification, can enhance the surface charge distribution and chelating capacity. For instance, MG-modified pine sawdust biochar adsorbs PS microplastics through electrostatic interaction. Relevant adsorption kinetics analysis shows that the maximum adsorption capacity of MG-modified pine sawdust biochar can reach 374.57 mg/g[14]. Table 1 shows the current research status of different modified biochar.

Table 1. Research Status of Different Modified Biochar

Formic acid-modified biochar	Formic acid activation pretreatment, nitrogen gas atmosphere pyrolysis	Polyethylene microparticles (1μm)	Faster	Langmuir, Freundlich model	Pseudo-first-order and pseudo-second-order dynamic models	[15]
Filamentous algal modified biochar	Pyrolysis of filamentous algae, modification by iron-loaded hydrothermal method	Polystyrene microplastic (PS)	24h	Langmuir model	Pseudo-second-order dynamic model	[16]
Phosphoric acid-modified Camellia oleifera fruit shell biochar	Phosphoric acid impregnation, pyrolysis under anaerobic conditions	Neodymium (Nd^{3+})	6h	Langmuir model($R^2=0.994$)	Quasi-second-order dynamic model	[17]
Magnesium-modified biochar	Impregnation with magnesium salt solution and pyrolysis	Exchangeable acids (H^+, Al^{3+}) in acidified tea garden soil	-	-	-	[18]
β -cyclodextrin modified biochar	Hydrothermal reaction, short-term activation, loading β -cyclodextrin	Copper ion (Cu^{2+})	12h	Langmuir model	Quasi-first-order dynamic model	[19]
Magnetically modified biochar	Prepared by impregnation with ferric chloride solution and liquid-phase reduction method	Microplastic	4h	Langmuir model($R^2=0.98$)	Quasi-second-order dynamic model	[20]

Studies have shown that the adsorption capacity of 50 nm PS (18 mg/g) is 125% higher than that of 1 μm particles (8 mg/g). Fibrous microplastics (such as PET) are more likely to be retained by macropores through physical entanglement due to their high aspect ratio. However, high-concentration microplastics will increase the competition for adsorption sites, but the overall adsorption capacity increases with the increase of concentration [14].

The pH value in the environment affects the electrostatic interaction between biochar and microplastics by regulating the surface charge of biochar and the ζ potential of microplastics. Under acidic conditions, the oxygen-containing functional groups (such as -COOH, -OH) on the surface of biochar undergo protonation, enhancing the electrostatic attraction to negatively charged microplastics. For example, the adsorption capacity of PET by sludge biochar at pH=4 is 65% higher than that at pH=9 [14]. Under alkaline conditions, the deprotonation of functional groups leads to an increase in the negative charge density on the surface of biochar, generating electrostatic repulsion with negatively charged microplastics and resulting in a decrease in adsorption efficiency. Meanwhile, OH^- may compete with hydrogen bonds formed on the surface of microplastics, further inhibiting adsorption [21]. The types and concentrations of ions in the solution change the adsorption behavior through the charge shielding effect or competitive adsorption. Low concentrations of Cl^- reduce electrostatic repulsion by compressing the double electric layer, promoting the contact between microplastics and biochar. High concentrations of SO_4^{2-} compete with microplastics for adsorption sites through anions (such as SO_4^{2-}), resulting in a decrease in adsorption capacity. Meanwhile, the strong ionic strength may disrupt the hydrophobic effect and reduce the adsorption efficiency of non-polar microplastics (such as PE) [21]. The ionic effect has a relatively small influence on physical adsorption (such as pore filling), but has a significant regulatory effect on chemical adsorption (such as electrostatic interaction and hydrogen bonding).

Dissolved organic carbon, heavy metals, or other pollutants in the solution may also affect adsorption through various pathways. The friction between microplastics and biochar releases DOC, forming microplastic-biochar heterogeneous aggregates, increasing the particle size of the adsorbent, and thereby enhancing the synergistic adsorption capacity for antibiotics [22]. The aromatic compounds in DOC may occupy the active sites on the surface of biochar, inhibiting the adsorption of microplastics. When heavy metals form complex pollutants with microplastics, the adsorption path can be changed through surface complexation or charge neutralization. For example, the adsorption capacity of Cu-PS composite particles decreased by 50% compared with pure PS [23]. The modified functional groups (such as -SH, $-NH_2$) on the surface of biochar can chelate with heavy metals, indirectly affecting the adsorption site distribution of microplastics [24]

An increase in temperature usually accelerates the adsorption kinetics, but it may reduce the equilibrium adsorption capacity. For example, the adsorption equilibrium time of PS by pine sawdust biochar at 30°C was shortened to 4 hours, but the maximum adsorption capacity decreased by approximately 10% compared with that at 20°C [21].

Organic matter content: The humic acid in the leachate of high-organic soil may compete with microplastics for adsorption through hydrophobic distribution, reducing the retention efficiency of biochar [25].

The ideas for optimizing the inherent properties of the material include adjusting the pyrolysis temperature, and using acid treatment and other processes to enhance porosity and the activity of surface functional groups. The environmental adaptability can be regulated by pH through different types of microplastics. Under acidic conditions, the electrostatic adsorption effect will be enhanced, while under alkaline conditions, microplastics with strong hydrophobic effects are more easily adsorbed. And through pretreatment, some organic matter in the soil is removed, the occupation of biochar adsorption sites by other pollutants is reduced, and the adsorption efficiency of microplastics is improved.

5. Future Outlook

At present, the directions that have been studied more on improving the adsorption performance of microplastics by biochar include the use of acid and alkali treatment to increase the surface oxygen-containing functional groups; Changing the pyrolysis conditions to expand pores, increase adsorption capacity and modify by combining metal ions to enhance the synergistic effect, etc. In the future, it can be considered to develop biochar composite materials, such as combining them with natural minerals to enhance adsorption capacity and selectivity. Or green modification technologies can be adopted to reduce the risk of chemical pollution. For instance, biochar can be treated with biological enzymes, and polyester-based microplastics can be partially degraded by hydrolases to produce rough surfaces or small molecule fragments, thereby increasing the retention efficiency of biochar pores. Or through enzymatic oxidation reactions, polar groups can be introduced onto the surface of microplastics to enhance their hydrogen bonds or electrostatic bonding with the functional groups on the surface of biochar. It can also be combined with phytoremediation or microbial degradation to achieve the synergistic treatment of microplastics and heavy metals in the soil.

6. Conclusion

This thesis mainly analyzes the adsorption mechanism of biochar on microplastics and its influencing factors and looks forward to the subsequent research directions for improving the adsorption performance. Biochar, as a porous carbonaceous material, has shown remarkable potential in the treatment of soil microplastic pollution due to its high specific surface area, rich surface functional groups and stable pore structure. It effectively adsorbs microplastics through dual mechanisms of physical retention and chemical combination, reduces their bioavailability and mobility, and thereby alleviates the ecological risks to soil microorganisms, crop roots and the food chain. The adsorption efficiency of biochar is jointly influenced by the pore characteristics of biochar, the hydrophobicity of microplastics and environmental conditions. Its adsorption performance and recovery convenience can be further enhanced through optimization of pyrolysis temperature, acid modification or functional loading. However, the current research on the adsorption of microplastics by biochar still faces challenges such as insufficient field validation and an unclear mechanism of multi-pollutant synergy. In the future, it is still necessary to focus on the innovation of materials, the integration of technologies, and interdisciplinary collaboration, establish standardized repair solutions, and promote large-scale applications.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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