Environment

# Adsorption-Desorption Behavior and Pesticide Bioavailability of Biochar in Soil

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**Biochar is a porous carbon-rich substance generated by anoxic pyrolysis of biomass. Biochar has a high adsorption capacity for organic contaminants in water and soil environmental media due to its large specific surface area and surface physical and chemical characteristics. The effects of biochar application on the adsorption-desorption behavior and bioavailability of pesticides in soil are illustrated in this paper; biochar can strongly adsorb pesticides in soil due to its loose and porous properties, large specific surface area and surface energy, and highly aromatic structure. Residual pesticide pollutants are reduced, as is desorption hysteresis, which reduces pesticide desorption. Furthermore, the use of biochar reduced the absorption and efficacy of pesticides in soil. At the same time, it describes the present gaps in research on the influence of biochar on pesticide migration mechanisms and its application in pesticide pollution control, and it identifies the major scientific issues that need to be addressed. Finally, the potential application of biochar in pesticide pollution management is discussed.**

**Keywords**: Biochar; Pesticide; Adsorption; Desorption; Bioavailability

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SOIL is one of the most important natural resources on which humans rely for survival and growth. The widespread, excessive, and irrational use of pesticides, in particular, has resulted in pesticide residues in the soil exceeding the soil's self-purification capability, resulting in soil pollution (1). Pesticides leaching and migration can pollute groundwater and surface water, threatening food safety, human health, and the ecological environment (2, 3).

Soil pollution control and remediation is frequently a lengthy process, and a variety of adsorbents are utilized to adsorb and fix pollutants in the soil (4). Biochar has become a hotspot in recent years as a novel type of environmental useful material. It is created via pyrolysis and carbonization of waste biomass at very low temperatures (about 700 ℃) and under total or partial anoxic conditions and is a type of carbon-rich charcoal with stable characteristics and microporosity (5, 6). Crop straw, fruit stones, forest falling waste branches, bagasse, soybean meal, cattle and poultry manure, and other biomasses are utilized as raw materials. When waste biomass thermal cracking is used to make biochar, not only biochar but also mixed gas and bio-oil can be obtained, and further processing can be used to produce hydrogen and other chemical products, reducing the impact on fossil-based energy and raw materials to some level (7). When applied to soil, biochar can fix carbon, retain fertilizer, keep water, and promote crop yield growth, as well as strongly adsorb organic pollutants like pesticides, herbicides, PAHs (polycyclic aromatic hydrocarbons), DDT, and Cd, Pb, and other heavy metal pollutants to reduce farmland pollution (8). At the moment, studies focus on heavy metal adsorption, while organic adsorption focuses on hydrophobic chemical compounds such as PAHs. Biochar stored in the soil can also trap carbon, as well as lower greenhouse gas emissions in the field such as carbon dioxide, methane, and nitric oxide, thereby decreasing global warming (9-11). The incorporation of biochar into the soil environment would undoubtedly impact the environmental behavior of numerous contaminants in the soil, and thus the fate of pollutants in the environment (12). Biochar has been proven to have tremendous promise in the prevention and restoration of organic pollution in soil and aquatic environments. We herein review the progress of biochar and its application in the control of pesticide pollution in soil, focusing on the adsorption-desorption behavior and bioavailability (microbial degradation) of pesticide pollutants in soil by biochar, pointed out the deficiencies in current research and the scientific questions that need to be answered urgently, and finally prospected the application.

## Biochar's Adsorption-Desorption Effect on Pesticide Behavior in Soil

### Pesticide Adsorption Mechanism in Biochar

The unique physical and chemical features of biochar allow it to strongly absorb organic contaminants in soil. To begin with, the rich pore structure inside biochar particles results in a bigger surface area and increased surface energy (13). Accordingly, after 1 hour of pyrolysis and carbonization at 850 ℃, the specific surface areas of bamboo charcoal and coconut shell charcoal were 370 and 410, respectively (14). Studies showed that biochar produced at higher temperatures has greater pollution remediation potential; nevertheless, when the pyrolysis temperature exceeds 400 ℃, the specific surface area declines with increasing temperature (15). First, the surface area of biochar increases with increasing pyrolysis temperature in the range of 300 ℃ to 600 ℃, however the surface area of biochar prepared at 700 ℃ is lower than that prepared at 600 ℃ (16). Second, in terms of element composition, biochar is primarily constituted of carbon, oxygen, hydrogen, and other elements, with high carbon content (about 70%-80%) (17). Biochar produced by pyrolyzing air-dried wood chips at 450 ℃ and 850 ℃ had carbon contents of 65.1% and 86.1%, respectively (18). Regarding surface chemical characteristics, biochar has a large number of aliphatic double bonds and diverse aromatized structural features, which increases its adsorption ability for organic contaminants with high hydrophobicity (including many pesticides) (19). As per some investigations, biochar has a composite structure composed of amorphous organic matter, inorganic minerals, and crystalline organic matter (20). The surface is covered by inorganic minerals with a high cation exchange capacity, similar to clay minerals, and the concentration of free OH- in the solution rises, as does the pH of the system (21), which might hasten the hydrolysis of organophosphorus pesticides (22) and carbamate pesticides (23). If biochar was aged for two years, the immobilization impact on triazine pesticides (simazine) did not alter significantly, indicating that biochar use is ongoing (24). Biochar is stable, has a long half-life, and is difficult to absorb due to its high carbonaceous and aromatized structure (25). Decomposition and mineralization, along with the progressive disintegration of the pesticides themselves, allow biochar to perform a long-term role in soil pollution prevention (26).

In short, biochar has unique surface physical and chemical properties as a good adsorption material, such as loose and porous, large specific surface area and surface energy, surface functional groups such as carboxyl, phenolic hydroxyl, acid anhydride, and other groups, and its own high aromatization structure.

### Adsorption Qualities of High Grade Can Strongly Absorb Organic Contaminants in the Soil

The surface adsorption and diffusion processes of biochar are two distinct processes (27). Surface adsorption occurs because the functional groups on the surface can establish stable chemical interactions with ions or organic substances (28). The physical and chemical properties and structure of the biochar surface fluctuate dramatically due to the varied pyrolysis temperatures, and surface adsorption increases with increasing carbonization temperature. Low-temperature biochar includes more organic components, and the partitioning effect is important (29). The hysteresis of organic pollutant adsorption and desorption by biochar is determined by structural characteristics such as specific surface area, pore structure, and aromaticity of biochar, as well as the molecular size, hydrophobicity, and pH value of the organic pollutant's environment (30). It is difficult for molecular organic matter to enter the biochar's loose and porous internal structure to adsorb, and polar chemicals can be powerfully adsorbed on biochar via the electron donor-acceptor interaction (31, 32).

## The Effect of Biochar on Pesticide Adsorption in Soil

Biochar operates on the soil to improve its adsorption capacity and strength for organic compounds, particularly hydrophobic organic pollutants such as PAHs, PCBs (polychlorinated biphenyls), and PCDDs (polychlorinated diphenyls), benzo-p-dioxin, pesticides, MCPA (dimethyltetrachloride), and other chemicals have an adsorption affinity many orders of magnitude larger than that of soil organic matter (33), and can be strongly adsorbed with a substantial adsorption capacity and significant nonlinear characteristics (34).

The physical and chemical properties of biochar is associated with the preparation raw materials, preparation temperature, and particle size, and the soil parameters and the qualities of target pollutants all have a significant impact on the adsorption behavior of biochar on organic pollutants. After pyrolyzing carbonized cow dung at 200 ℃ and 350 ℃ to make biochar BC200 and BC350, respectively, and studied the adsorption efficiency of them and biomass raw materials (BC25) on the pollutant atrazine in soil, discovering that biochar is more effective than biomass raw materials (35). In another study, the ash produced by burning air-dried wheat and rice straw residues (the major component of biochar) was added to the soil, and the ash-added soil was tested for the pesticide Diuron adsorption capability. The ash concentration in the soil was found to be 0-6ppm. When the amount of ash applied surpasses 0.05%, the soil's Diuron adsorption capacity is 400-2500 times that of the control soil. A modest amount of ash can significantly boost the adsorption capability of organic contaminants (36). Through using a batch balance test, the adsorption properties of simazine and atrazine by biochar made from wood and bark of maple, elm, and oak pyrolyzed at 450 ℃ was tested, and discovered that the time required for biochar adsorption of pesticides with different particle sizes to reach equilibrium is different. When the particle size is 0.075 mm, it took one day to attain equilibrium; when the particle size is 0.025 mm, it takes up to five days. Furthermore, the adsorption capacity of biochar increases as the solid/liquid ratio decreases; when the pH value is less than 7, the adsorption capacity decreases as the pH value of the solution increases; when the pH value is greater than 7, the relationship between adsorption capacity and pH is not significant (37). Pesticide adsorption and immobilization change when biochar is added to different soils. By adding 0.5% biochar derived from red gum pyrolysis and carbonization at 450 ℃ to red soil, paddy soil, and black soil, it greatly improved acetamiprid adsorption. The contribution of 0.5% addition ratio to acetamiprid adsorption in the three soils was 52.3% in red soil, 27.4% in paddy soil, and 11.6% in black soil, with red soil having the largest contribution (38). This shows that the effect of biochar is stronger in soils with low organic matter content, because the high organic matter content can clog the pores of biochar or compete with it for adsorption sites. Therefore, the adsorption of organic pollutants such as pesticides in soil on biochar is nonlinear, and as soil carbon content increases, so does the adsorption capacity and adsorption strength of pollutants (39).

## The Effects of Biochar on Pesticide Desorption in Soil

If pesticides and other pollutants in the soil are desorbed and released, they will be absorbed by plants, infiltrate surface and groundwater, and eventually pollute the environment (40). As a result, investigating pesticide desorption behavior in soil has a favorable impact on pesticide pollution control in soil. The desorption process of pesticides will be hysteresis in both natural soil and soil treated with biochar, with the latter being more substantial, which is beneficial to lowering the desorption of pesticides and reducing the solubility of pesticides (41, 42). The desorption isotherms of Diuron and atrazine displayed obvious hysteresis when compared to the adsorption isotherms after adding biochar made from poultry dung to the soil at 550 ℃ (43). Yu et al. investigated the adsorption-desorption behavior of diuron on natural soil and black carbon-applied soil using the batch oscillation method and serial dilution method and discovered that both the adsorption and desorption isotherms displayed apparent hysteresis (44). The diuron hysteresis coefficient H is 1.14, and as the concentration of black carbon added to the soil grows from 0.1% to 1.0%, the H value rapidly increases from 1.32 to 14.92, indicating that it is compatible with nature. The adsorption-desorption hysteresis behavior of pesticides was more visible after adding black carbon to soil, and the higher the black carbon content, the more obvious the desorption hysteresis (45). The hypothesis of "micropore adjustment effect" explains desorption hysteresis (46). Accordingly, micropore adsorption is the direct cause of desorption hysteresis. On the one hand, the pollutant molecules in the solution enlarge the micropores through thermodynamic action, adding a new internal solid-phase adsorption surface during the adsorption process. On the other hand, contaminants can enter micropores via active diffusion, increasing the diameter of the micropores and inducing deformation of the surrounding micropores. The pollutant molecules leave the filled micropores during the desorption process, and the surrounding micropores cannot quickly return to their normal condition to release the adsorbed pollutant molecules, resulting in a portion of the adsorbed pollutant molecules being unable to be desorbed.

As a result, adsorption and desorption of contaminants occur in different physical states, which is the primary cause of desorption hysteresis. Furthermore, because biochar has a rich micropore structure, more pesticide molecules are absorbed by the micropores and are not easily released, resulting in greater desorption hysteresis (47). However, the explanation needs to be investigated further.

## The Effects of Biochar Application on Pesticide Bioavailability in Soil

The high adsorption of biochar to pesticides and herbicides in soil would inevitably impact their bioavailability (microbial degradation utilization and plant absorption) and therapeutic efficacy (killing of target plants, dangerous microbes, and pests). The ability of pesticides and other chemical substances in soil to be biologically utilized is referred to as bioavailability, and the adsorption capacity of biochar will certainly affect the bioavailability of organic pollutants (48). Yu et al. pyrolyzed two types of biochar at 450 ℃ and 850 ℃, respectively, and investigated the effects of biochar application on the breakdown of pesticides chlorpyrifos and carbofuran, as well as the absorption of pesticides by green onions (49). The results showed that as the quantity of biochar increased, so did the breakdown of pesticides by microorganisms and the absorption of pesticides by green onions. After 35 days, 86%-88% of pesticides in soil without biochar decomposed, while only 51% of carbofuran and 44% of pesticides in soil with 1.0% biochar prepared at 850 chlorpyrifos decayed. At the same time, it was discovered that in soil with 1% biochar, the content of the two pesticides in shallots reduced by 10% (chlorpyrifos) and 25% (carbofuran), respectively, as compared to soil without biochar, demonstrating that biochar has an anti-pesticide effect. The combined effect of the two pesticides reduced their bioavailability. Yu Xiangyang et al. investigated the influence of pesticides on the killing effectiveness of target plants and pests by applying biochar made from wheat and rice straw to the soil and discovered that the herbicides Diuron (50) and clomazone (51) were successful in destroying weeds, but the efficacy has been reduced. In other words, pesticide absorption by target plants and pests is relatively low, reducing pesticidal efficacy. The application of biochar to the soil reduces the pesticides and other organic substances in the soil that are decomposed by microorganisms and absorbed by plants, hence reducing organic pollutants' bioavailability. Simultaneously, because the pesticide is firmly adsorbed on the biochar, the efficacy of killing target plants and pests is diminished.

## Inadequacies and Significant Scientific Concerns Should be Addressed

Studies are increasingly interested in biochar as an adsorbent due to its high adsorption performance on contaminants in soil. The effect of hydrolyzed biochar on pesticide adsorption-desorption, degradation, and migration was discovered, revealing that biochar can substantially adsorb pollutants and limit their leaching migration. Biochar application can induce significant changes in the biological, physical, and chemical aspects of soil, which can alter pesticide absorption. The nature of the biochar itself, soil type, farming use, and the nature of the target pesticide all have an impact on this effect. At the moment, research on the movement and transformation of pesticides in soil by biochar is still in its early stages, and there are many gaps and crucial scientific questions that remain unanswered,

i. The use of biochar reduces the killing efficacy of pesticides on target plants and pests. Additionally, pesticide pollutants are fixed in the soil, increasing the half-life of pesticides in soil and causing adverse effects. It remains to be seen how these issues will be resolved.

ii. The majority of existing studies are short-term laboratory batch balance and soil column experiments after several months or 1-2 years of stable aging after biochar addition. Therefore, there is lack of long-term field plots, particularly large-scale (slope surface, catchment area) system.

iii. When it comes to the effect of biochar on pesticide adsorption, traditional research typically involves batch equilibrium tests under saturated soil conditions, and the measured solid-liquid two-phase partition coefficients are frequently larger than the actual ones. The unsaturated transient flow experiment (a subset of the batch balance test) can be used to investigate the adsorption of metal ions and organic contaminants with relatively high hydrophilicity in soil under unsaturated water conditions. It would be useful to investigate the adsorption and desorption processes of pesticides in biochar-enriched soil, in order to get pesticide adsorption and desorption amounts closer to the actual field circumstances. However, because the experimental steps for the unsaturated transient flow experiment are slightly more involved than those for the batch equilibrium experiment, there have been few relevant investigations to date.

## Conclusion

Biochar has been shown to strongly adsorb pesticidal pollutants in soil, improve desorption hysteresis, reduce pesticide desorption amount, and reduce pesticide soluble concentration. Excessive and inappropriate pesticide use resulted in non-point source pollution of soil and water, and the impact of biochar made from different raw materials varies. However, studies on the coupled effects of biochar application on the biological, physical, and chemical processes of the soil environment is still lacking, and it is necessary to find the best balance between the two aspects of drug efficacy, comprehensively evaluate, and systematically develop biochar-oriented preparation and optimized application technologies suitable for different soils and pesticides are needed. Biochar application to soil is an irreversible procedure, and its high stability allows it to remain in the soil for an extended period of time. How can we conduct tracking experiments or mimic its transformation process in soil, as well as conduct a comprehensive study on biochar and its immobilized pesticides still require further investigation. Future studies need to investigate the mechanism and regulation principle of biochar's cooperative action with organic and inorganic fertilizers such as compost and nitrogen fertilizer, as well as how to prevent the potential adverse effects of biochar use. There are also other issues that must be addressed in terms of practical applicability. Global incentive programs are required for the study and development of biochar pollution control materials and technology. Development of scientific and safe biochar dosing technology is expected to control weeds and pests to ensure agricultural production, effectively prevent and control non-point source pesticide pollution, and protect the ecological environment by optimizing the preparation process and product performance of biochar.■

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