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The Application of Invasive Plant-Derived Biochar in Controlling Plant Invasion by Removing its Allelochemicals

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Abstract

Invasive plants seriously threaten the natural ecosystem and human health due to their strong ecological adaptability, reproduction, and diffusion ability, so that the utilization and control of invasive plants have attracted much attention. Biochar is widely used in environmental and soil remediation owing to its high aromaticity and anti-degradation ability. However, the research on biochar prepared by invasive plants to adsorb their own allelochemicals is still scarce, which may limit the application of biochar in invasion prevention and control. In this paper, the application of invasive plant-derived biochar (IPB) and the adsorption effect and mechanism of IPB and its composites on organic and inorganic pollutants are reviewed, which may enhance our understanding for the utilization of invasive plants and the restoration of local plant communities.

Keywords: Invasive plant; Biochar, HAP; Adsorption; Intrusion prevention

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1. Invasive Plants and Their Management

1.1 Hazards and Invasion Mechanisms of Invasive Plants

Invasive plants refer to non-local plants that can rapidly grow and reproduce in the invaded state, and seriously destroy the local ecosystem (Wang, 2010). They can invade various ecosystems including woodland, farmland, water, wetland, grassland, and urban green space, leading to their wide distribution worldwide (Basu et al., 2004; Long et al., 2017). After the successful invasion, a large area of single superior community can be formed, posing a serious threat to the growth and survival of local animals and plants, reducing biodiversity, and destabilizing the local natural ecosystem (Yang et al., 2002). Moreover, plant invasion may result in the destruction of genetic diversity among local species or the release of numerous allergens, which will seize the living space of local economic species and cause more allergic reactions (Xu et al., 2019).

The success of invasive plant invasion depends on the invasiveness of invasive plants and the invasibility of habitats (Geng et al., 2004). Previous studies have put forward possible mechanisms and hypotheses from different angles. For instance, the "propagule pressure hypothesis" posits that the introduction of a large number of reproductive propagules, repeatedly, enhances the likelihood of successful invasion (Li et al., 2020). Other hypotheses based on the relationship between invasive and local species include the "enemy release hypothesis," the "novel weapons hypothesis," and the "increased competitive ability hypothesis." Additionally, there are hypotheses that consider habitat suitability for invasion, such as the "empty niche hypothesis" and the "diversity resistance hypothesis" (Wang et al., 2014). Among them, the new weapon hypothesis is one of the most important mechanisms for the successful invasion of invasive plants, which holds that invasive plants will release allelochemicals including α-pinene, β-pinene, 4-terpenol etc. into the environment through volatilization of stems and leaves, leaching, root secretion and decomposition of plant residues, thus inhibiting the seed germination and plant growth of surrounding plants and enhancing their invasiveness (Li et al., 2020; Li et al., 2006; Callaway et al., 2004). A large number of studies have proved that allelochemicals are often organic compounds such as phenols, terpenes and alkaloids (Yan et al., 2020), these compounds refer to allelopathic chemicals, mostly plant secondary metabolic compounds, which mainly enter the soil to affect the growth and development of themselves or neighboring plants. For example, the extracts of *Xanthium strumarium* have significant inhibitory effects on germination rate and root length of *Setaria viridis*, *ryegrass*, *lettuce* and *pakchoi* (Yuan et al., 2017). The research findings on the allelopathic effects of *Solidago canadensis* litters on the seed germination and seedling growth demonstrate a significant inhibition caused by the *S. canadensis* litters. (Hu et al., 2020). The long-term accumulation of these organic substances leads to soil poisoning, and even if invasive plants are removed, this "legacy effect" may exist for a long time and affect local plant communities (Lu et al., 2004; Yu et al., 2020). This poses a great challenge to the restoration of local plant communities. Therefore, it is necessary to remove these allelochemicals, which can not only reduce the diffusion trend of invasive plants, but also benefit restoration of local plant communities.

1.2 Methods For the Control and Management of Invasive Plant

At present, the main control methods of invasive plants include physical control, chemical control, and biological control (Wang et al., 2009). Physical control is a method of pest management that utilizes physical factors or mechanical actions to disrupt the growth, development, and reproduction of organisms, thus preventing and controlling the spread of harmful pests. While this approach may not completely eradicate invasive species, it exhibits rapid efficacy through artificial intervention, albeit at the expense of considerable human and material resources (Wang, 2019). Chemical control involves the use of toxic chemical agents to prevent and control the targeted organisms (Wang, 2019). It offers advantages such as labour savings, prompt and effective weed control, ease of use, and suitability for large-scale application. However, the cost of chemical control is high, and it is often uneconomical to use in large-scale and low-economic ecological environments, and it is still limited in special environments such as reservoirs and lakes (Jiang et al., 2006). Biological control is to use one organism to inhibit another organism, and to use the interaction between organisms to control organisms. Although there is no chemical pollution in biological control, the effect is slow (Wang et al., 2019). Biochar is widely used in environmental remediation and soil remediation because of its excellent characteristics such as wide source of raw materials, low cost, large specific surface area and abundant surface functional groups (Wu et al., 2020). Biochar produced from invasive plant species offers higher added value compared to conventional raw materials such as corn stalks and cottonseed shells. By converting invasive plant biomass into biochar, not only can the spread of invasive plants be curbed, but waste materials can also be utilized effectively. Therefore, invasive plant-derived biochar (IPB) has been widely concerned by biologists and ecologists (Feng et al., 2021).

Table 1. Comparison of main control methods of invasive plants

Main Control Methods of Invasive Plants	Advantage	Disadvantage
Physical control	rapid and accurate	not completely, Consume a lot of manpower and material resources
Chemical control	labour savings, prompt and effective, ease of use, and suitability for large-scale application.	High cost, limited in special environments
Biological control	no chemical pollution	the effect is slow

At present, invasive plants are widely used for animal feed, compost, fuel and biological pesticides, etc., but little research focused on the biochar prepared by invasive plants and evaluate its adsorption capacity of removing heavy metals and organic pollutants. Moreover, less research use IPB to prevent and control invasive plants. Li et al. (2017) concluded that biochar can alleviate the toxic effect of allelochemicals (Catechol, resorcinol) on tomato seedlings. Jillian et al. (2022) also proposed that biochar treatment of allelopathic plant extracts significantly reduced the effect on seed germination of *Garlic* and *Melilotus*. Adding biochar to soil can effectively reduce the toxicity of allelochemicals to plant growth (Prapagdee et al., 2003). Zhang et al. (2018) used biochar prepared by *S. canadensis* to adsorb allelochemicals dimethyl phthalate and found that the germination of tomato seedlings recovered significantly after adding biochar, but which was affected by pyrolysis temperature and residence time. It has also been proved that biochar can alleviate toxic effects of allelochemicals because biochar can adsorb or isolate allelochemicals (Paranavithana et al., 2016; Butnan et al., 2015; Peake et al., 2014; Yan Yu, 2014). Therefore, using IPB to adsorb allelochemicals may become a potential and available method to control plant invasion.

2. Invasive Plant-Derived Biochar

2.1 Structure and Adsorption Mechanism of Biochar

Biochar, derived from animal and plant wastes, straws, rice husks, and animal manure, generally refers to a carbonized substance with high carbon content (>70%) and a rich porous structure obtained through the slow pyrolysis of organic biomass under hypoxic conditions or a combination of hypoxia and high temperature. (Li et al., 2011; Guo et al., 2020). Biochar exhibits a remarkably high carbon content ranging from 30% to 90%. It possesses a large specific surface area and abundant pore structure, enhancing its capability to adsorb heavy metals and organic matter effectively. Biochar typically has an alkaline pH ranging from 5 to 12, with an average pH of 9.15. Biochar is rich in functional groups such as phenolic groups, carboxylic acids, alcohols, ketones, aldehydes, ethers, and aromatic structures, which enable it to adsorb hydrogen ions in soil and thereby improve acidic soil conditions. (Ma et al., 2020). The abundant structural characteristics of biochar provide numerous active sites for the adsorption of pollutants. Its adsorption mechanism generally includes surface adsorption, partition, π-π electron giving and receiving, etc. The surface adsorption includes physical adsorption (van der Waals force, hydrogen bond, electron giving and receiving), chemical adsorption, and pore filling effect (Aljeboni et al., 2014; Li et al., 2017). In addition, there is usually π-π interaction between the dense aromatic ring structure and organic matter, and the partition is also the main removal mechanism of aromatic pollutants (Lee et al., 2015; Verma et al., 2017). In the actual reaction, there are usually many mechanisms involved in the adsorption process of organic pollutants by biochar. Zhao et al. (2015) identified pore filling, π-π interactions, and hydrogen bonding as key mechanisms in the adsorption of florfenicol by magnetic biochar and reed biochar. Miao et al. (2020) found that biochar can remove heavy metals through ion exchange, surface adsorption, functional group complexation and precipitation formation, and showed certain removal effects on lead, cadmium, zinc, copper and chromium. The adsorption of NH_4^+-N by biochar is a monolayer chemisorption, electrostatic attraction, cation exchange and surface complexation in the adsorption process (Chen et al., 2020; Wu et al., 2020; Li et al., 2020; Qian et al., 2020).In summary,Biochar has the characteristics of high carbon content, active functional groups, porous structure, good stability and large specific surface area, which make biochar have good adsorption capacity (Fan et al., 2016; Lonappan et al., 2016).

2.2 Adsorption Application of Invasive Plant-Derived Biochar

IPB can save production costs and improve the biological value of invasive plants, so it is widely used in the fields of environment, agriculture, and energy (Feng et al., 2021). With the rapid development of industrialization, a large number of high-concentration heavy metals and organic wastewater have seriously polluted water and soil environment. Biochar, with its low cost, rich pore structure, and large specific surface area, has become the primary adsorbent for removing water and soil pollutants, making adsorption one of the effective methods for eliminating these pollutants. (Li et al., 2019; Luo et al., 2018). Considering the ecological problems caused by invasive plants, the preparation of biochar from invasive plants for the removal of heavy metals and organics can be used to treat waste with waste. For example, *S. canadensis* biochar prepared at 450 °C has the best adsorption effect on Cd^{2+} (Tang et al., 2019). Biochar from five invasive plants (*Bidens pilosa*, *Praxelis clematidea*, *Ipomoea cairica*, *Mikania micrantha*, *Lantana camara*) prepared at 500 °C has better removal effect on Cd^{2+} and Cu^{2+} than biochar prepared from other raw materials such as crop straw. *B. pilosa* and *P. clematidea* biochar have the best removal effect on Cd^{2+}, with the maximum adsorption capacity reaching 167.22 mg/g and 141.84 mg/g, respectively. Biochar of *B. pilosa* and *M. micrantha* has the best removal effect on Cu^{2+}, with the maximum adsorption capacity reaching 67.75 mg/g and 62.27 mg/g respectively (Zhao et al., 2019). The removal of Cd (II) from invasive plant *Spartina alterniflora* biochar prepared at 700 ℃ was 11.6 mg/g; Biochar prepared from invasive plants (*Prosopis juliflora*, Alternanthera philoxeroides and *Ambrosia tirfida L*) has a higher adsorption capacity for Pb (II) than traditional biochar (Feng et al., 2021), which is 43.0 mg/g, 257.1 mg/g and 333.3 mg/g, respectively. In addition, pyrolyzed *ragweed* biochar has low polarity, high aromaticity, and large specific surface area, so it has a nice adsorption capacity for organic pollutant trichloroethylene (Ahmad et al., 2014). In soil remediation, invasive plant biochar is often used to adsorb pollutants such as herbicides or antibiotics, which is a promising way. Biochar from invasive plant *Sicyos angulatus* produced by pyrolysis at 700 ℃, has high aromaticity and hydrophobicity, so it has a good adsorption rate for sulfamethazine in soil, and can be widely used to remove this antibiotic in soil (Vithanage et al., 2014; Rajapaksha et al., 2015). In addition, the co-pyrolysis of pig manure and invasive plant *Polygonum cuspidatum* increased the fixed carbon content of the combined raw material biochar obtained at 600 ℃ by nearly 1.5 times, and all the combined raw materials biochar met the requirements of soil improvement and carbon sequestration (jing et al., 2022).

3. Modification of Invasive Plant-Derived Biochar

3.1 Preparation and Modification of Biochar

The most common method to prepare biochar is pyrolysis (Jahirul et al, 2012). Pyrolysis conditions (temperature, heating rate, etc.) have a significant effect on the physicochemical properties of biochar (Mašek et al., 2013). During thermal decomposition, hemicellulose, cellulose and lignin (components of biomass) are cross-linked, depolymerized and cracked at their respective temperatures to produce solid, liquid and gaseous products (Cha et al, 2016). Preparation of biochar by pyrolysis has the advantages of simplicity and low cost (Lei et al., 2022). Due to the limited adsorption capacity of biochar for pollutants, many studies have focused on the surface modification of biochar in recent years (Jung et al., 2018). Acid-base modification is a chemical modification method. Treating raw materials or biochar with acid and alkali reagents increases the surface oxygen-containing acidic or basic functional groups, active coordination sites and specific surface area of biochar (Huang et al., 2020). After modified by potassium permanganate solution, the increase of oxygen-containing functional groups enhances the ion exchange ability and complexation, which greatly improves the adsorption performance of Pb^{2+} and its adsorption removal rate can reach 80%. Oxidation modification can obviously increase the types and quantities of functional groups on the surface of biochar, such as hydroxyl, phenol and carboxyl, and enhance the hydrophilicity of biochar (Du et al., 2019). Organic modification mainly uses the interaction between specific organic matter and target matter to enhance adsorption capacity (Qian et al., 2020). Biochar was modified by polyethylenimine and glutaraldehyde. The cross-linking reaction between polyethylenimine and biochar surface made biochar rich in oxygen-containing functional groups, and the adsorption capacity of Cd^{2+} increased from 23.09 mg/g to 435.7 mg/g (Ma et al., 2014). UV radiation modification can improve the adsorption performance of biochar for metal ions, and its adsorption capacity for Pb^{2+} and Cd^{2+} increased to 136% and 25.3%, respectively (Chen, 2014). Clay mineral modification mainly uses clay minerals to impregnate biochar to change its composition and physical properties, thus improving its adsorption capacity for oxygen anions (such as PO_4^{3-}) and polyatomic cations (such as NH_4^+) (Tom et al., 2017). The biochar magnesium-aluminum hydrotalcite composites (Mg/Al-LDHs @ BC) were prepared by coprecipitation method. The adsorption kinetics of phosphate is more in line with the quasi-second-order kinetic model, and the isothermal adsorption process is more suitable for Langmuir model. The fitted maximum adsorption capacity is 71.37 mg/g, which is higher than Magnesium-aluminum hydrotalcite (Mg/Al-LDHs) and about 9 times higher than biochar (Cheng et al., 2021). The biochar composites (MFSL) modified by calcined magnesia-iron hydrotalcite were prepared by simple coprecipitation method with waste spinach leaves as biochar raw materials. The Langmuir model fitting showed that the maximum adsorption capacity of MFSL for phosphate could reach 115.10 mg/g, which was 75% higher than that of the original biochar (Nie et al., 2021). Metal oxide modification is usually carried out by soaking biochar or its raw materials in metal nitrate or chloride salt solution, and some metal modification can increase the potential of biochar's adsorption capacity for metal cations. The biochar of *Eichhornia crassipes*, a typical aquatic invasive plant in China, has a good passivation advantage for heavy metal ions in acid rain areas after loading iron (Pan et al., 2017). The biochar of *Eupatorium adenophora Spreng* was modified with Fe (III), and the adsorption effect of modified *E. adenophora* biochar on heavy metal Cr (VI) in aqueous solution was investigated. The experiment showed that Fe modification changed the adsorption process of *E. adenophora* biochar, and the maximum adsorption capacity of Fe modified *E. adenophora* biochar on Cr (VI) in water reached 70.40 mg/g, which was 1.77 times that before modification (Zhou, 2018). In soil remediation, steam activation is often used to modify biochar to avoid secondary pollution to soil. Therefore, composite materials should also choose environmentally friendly materials without secondary pollution.

Table 2. current research of using a modification of biochar

Modification Method	Introduction And Advantage
Acid-base modification	Treating raw materials or biochar with acid and alkali reagents increases the surface oxygen-containing acidic or basic functional groups, active coordination sites and specific surface area of biochar
Oxidation modification	obviously increase the types and quantities of functional groups on the surface of biochar, and enhance the hydrophilicity of biochar
Organic modification	uses the interaction between specific organic matter and target matter to enhance adsorption capacity
Modified by polyethylenimine and glutaraldehyde	The cross-linking reaction between polyethylenimine and biochar surface made biochar rich in oxygen-containing functional groups, Increase the adsorption capacity of Cd^{2+}
UV radiation modification	improve the adsorption performance of biochar for metal ions (Pb^{2+}, Cd^{2+})
Clay mineral modification	uses clay minerals to impregnate biochar to change its composition and physical properties, thus improving its adsorption capacity for oxygen anions (PO_4^{3-}) and polyatomic cations (NH_4^+)
Metal oxide modification	carried out by soaking biochar or its raw materials in metal nitrate or chloride salt solution, increase the potential of biochar's adsorption capacity for metal cations
steam activation modification	avoid secondary pollution to soil

3.2 Study on Biochar and Hydroxyapatite Composites

Hydroxyapatite (HAP) is the primary mineral component of vertebrate hard tissues (bones and teeth), widely occurring in nature. Due to its unique crystal structure, non-toxicity, biocompatibility, biodegradability, low water solubility, low cost, and high adsorption affinity for various heavy metals in aqueous media, HAP is considered an environmentally friendly adsorbent with significant potential for soil remediation applications (Yang et al., 2016). However, the high surface reactivity of HAP nanoparticles can cause aggregation in aqueous solutions due to van der Waals forces. This aggregation reduces water dispersibility and specific surface area, thereby diminishing the surface reactivity towards target pollutants (Yang et al., 2016; Li et al., 2018; Zhu et al., 2018).

Considering the advantages of biochar, it serves as an ideal medium for preventing the self-agglomeration of nano-hydroxyapatite and enhancing its capability to remove heavy metals from wastewater (Jung et al., 2019). Hydroxyapatite, with its unique crystal structure, exhibits strong adsorption affinity for divalent metal ions, is environmentally friendly, and poses minimal pollution risk. Modification of biochar with nano-hydroxyapatite has been shown to significantly enhance the adsorption of lead (Hu et al., 2012). Additionally, biochar effectively disperses nano-hydroxyapatite particles, preventing their agglomeration and thereby improving adsorption efficiency. Co-pyrolysis and high-temperature activation of biochar with hydroxyapatite result in enhanced pore width and permeability in corn straw carbon-hydroxyapatite composites. Walnut shell carbon-hydroxyapatite composites exhibit a more regular pore arrangement, larger pore sizes, and a higher distribution of small hydroxyapatite particles on their surfaces (Zhang et al., 2018). These modifications lead to a significant decrease in the available soil (DTPA) Cd content in most composites compared to single-passivation materials, indicating stronger Cd fixation capability likely due to increased pore and surface area of biochar post-activation (Liu et al., 2023).

The adsorption mechanism of biochar for heavy metals is generally not single, but several mechanisms interact with each other. Zhang et al., 2018 loaded nano-hydroxyapatite on the surface of biochar (BC) at high temperature and limited oxygen to prepare biochar-supported nano-hydroxyapatite (HAP/BC) composite. The adsorption effect of this composite on Pb^{2+} was investigated experimentally. The results showed that the adsorption effect of HAP/BC was better than BC, and its main adsorption mechanism was the dissolution-precipitation of nano-hydroxyapatite and the complexation of oxygen-containing functional groups such as-OH and-COOH on the surface of biochar. Zhu et al., 2017 compared the adsorption characteristics of biochar and biochar modified materials for copper and found that nano-hydroxyapatite improved the stability of biochar to some extent, and attached to the surface of biochar evenly, which improved the hydrophilicity of biochar. In addition to the complexation and precipitation of biochar itself, the oxygen-containing functional groups on the surface of composite materials provide π electrons, which can form a stable structure with copper ions during adsorption and improve the adsorption rate of copper ions.

4. Adsorption of Allelochemicals by Invasive Plant-Derived Biochar

Although the application of IPB has been concerned, its application in invasion prevention and control is still rare. For example, magnetically modified biochar of invasive plant *water hyacinth* can increase the adsorption of arsenic from 8.9% to 100% (Zhang et al., 2016). The degradation rate of 2, 4, 6-trichlorophenol by invasive plant *E. adenophorum* modified by bimetallic nano-iron/nickel increased by 39.7-71.6% (Liu et al., 2019). Most of these studies use invasive plant biochar to adsorb pollutants such as heavy metals or organic matter, and rarely study allelochemicals used to adsorb invasive plants. Only Zhang et al. (2018) used biochar prepared by *S. canadensis* as adsorbent and found that it has strong adsorption capacity for dimethyl phthalate (DMP), an allelochemicals of *S. canadensis*, with a maximum adsorption capacity of 59.37 mg/kg. Therefore, IPB can be used for invasion control and reduce the inhibitory effect of invasive plants on local plants. Of course, the adsorption capacity of pure biochar is limited, and modified biochar often has better adsorption effect. Therefore, in the future, we should not only strengthen the research on the adsorption effect of invasive plant biochar on allelochemicals but also explore the composite biochar with higher adsorption efficiency and environmental friendliness, which will have broad application prospects in environmental remediation.

5. Conclusion

Plant invasion poses a serious threat to natural ecosystem diversity and local economic development. The primary challenge lies in removing invasive plants without causing secondary pollution. Utilizing biochar to extract allelochemicals from invasive plants not only addresses the issue of excessive biomass but also reduces the invasive plants' ability to spread, potentially enhancing invasion prevention and control strategies. Research indicates that biochar can effectively adsorb allelochemicals, thereby mitigating the allelopathic effects of invasive plants. However, the effectiveness of this adsorption is somewhat limited. Nano-hydroxyapatite, a naturally abundant material with low cost and good stability, significantly enhances the adsorption capacity of biochar. While nano-hydroxyapatite has been extensively studied in biochar composites, further research is needed to optimize its ability to adsorb allelochemicals. Moreover, the efficiency of biochar composites in removing allelochemicals can vary depending on the invasive plant species, pyrolysis conditions, and reaction parameters. Therefore, future studies should focus on understanding how different invasive plant sources and pyrolysis methods influence the adsorption mechanisms of biochar. This targeted approach will help identify optimal biochar formulations for effectively mitigating allelopathy in invasive plants. In conclusion, advancing research in these areas holds promise for developing sustainable strategies to manage invasive plant species while minimizing environmental impact.

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Declaration of Conflicting Interests

All authors declare that they have no conflicts of interest.

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