

Preparation and Modification of Biochar and Application of Modified Biochar in Remediation of Contaminated Soil

Yixiao Duan *

Environmental Engineering, Nanjing University of Information Science and Technology, Nanjing, Jiangsu, 210044, China

* Corresponding Author Email: 1910631201@mail.sit.edu.cn

Abstract. Biochar, with its unique properties including high specific surface area, has become an increasingly popular material in the field of environmental restoration. The present paper provides a systematic analysis and summary of the preparation, characterization, and modification strategies for traditional biochar, as well as its application in soil remediation. A variety of different methods have been developed and applied to produce biochar, of which the most commonly used method is pyrolysis which consists mainly of slow and fast pyrolysis, followed by hydrothermal carbonization. Biochar can be modified by the injection of acids, alkalis, metal oxides, metal ions, steam and gas. On this basis, the utilization of modified biochar in soil restoration and remediation was further analyzed. Modified biochar breaks through various limitations such as the instability of traditional biochar, and performs an irreplaceable function not only in adsorption of organic pollutants, but also in the removal of heavy metal pollution. Additionally, managers also need to avoid the potential risk of secondary contamination by releasing polycyclic aromatic hydrocarbons (PAHs) into the surrounding environment. The aim of this paper is to explore the basic properties and preparation methods of biochar, to identify its restrictions and different modification methods, to highlight the contribution that modified biochar can make to today's sustainability-focused world, and to lay the groundwork for future research.

Keywords: Biochar; characteristics; modification; application; soil remediation.

1. Introduction

Biochar is a solid material rich in black carbon, produced by pyrolysis of biomass at high temperatures under anaerobic or oxygen-limited conditions. It is a stable substance with unique properties such as porous and multi-surface functional groups. Being a high-temperature material, it holds great potential for various applications [1]. Biochar has become an ideal adsorption material to replace activated carbon due to its advantages of wide source of raw materials, low cost and stable performance [2]. However, the long-term exposure of raw biochar to air will change its physicochemical properties and limit its ability to remove pollutants, so it needs to be activated and modified.

With the aim of improving the technical application of biochar, researchers are carrying out a great deal of research into its modification and are developing techniques that are tailored for different situations, with the aim of increasing the adsorption capacity and stability of biochar, and improving its effectiveness in cleaning up the environment. Biochar was prepared by Tu et al. [4] through a process of mixing dry sludge with FeSO_4 solution, followed by pyrolysis, and later soaking in HCl and HF solutions. The result was an increase in the specific surface area (SSA) of the biochar increased from $14 \text{ m}^2/\text{g}$ to $33 \text{ m}^2/\text{g}$ [4]. Biochar was prepared from corn stover by Zhang et al. [5], who then modified it using H_2O_2 . The modification resulted in the biochar having a 2.05-fold increase in specific surface area, as well as higher acidity and polarity. Zhao et al. [6] used H_3PO_4 to activate biochar and found that H_3PO_4 -modified biochar had a higher adsorption capacity for compound contaminants. Duca and colleagues produced steam-activated activated carbon from walnut shells and evaluated its ability to adsorb Sr from aqueous solutions [7].

This paper outlines the two most widely used methods of preparing biochar and elaborates on the properties of traditional biochar. It also summarizes the commonly used modification strategies for traditional biochar, which mainly include physical, chemical, and other methods of modification.

Furthermore, this paper presents the use of modified biochar for soil remediation to enhance soil physicochemical properties and pollutant adsorption. Overall, this paper aims to elucidate advances in the preparation, modification and application of biochar in soil remediation, providing valuable information for future research and development in the field. importance of environmental science.

2. Preparation and characterisation of biochar

Biochar is a solid substance that is rich in carbon, stable, insoluble, and aromatic. It is obtained from organic raw materials under specific thermal conditions in environments where there is limited or no oxygen [1, 2]. The feedstocks used to produce biochar are derived from carbon-rich biomass materials, mainly including agricultural, forestry and household wastes, as well as biomass with low cost components such as animals, plants and micro-organisms [2]. Examples include crop straw, wood chips, fruit shells, household waste, livestock manure, skeletons, algae and sewage sludge. In the production of biochar, feedstocks have different elemental composition ratios, which, when combined with different pyrolysis methods, result in biochar with different yields and properties. Feedstocks can be converted to char by carbonization processes including pyrolysis and hydrothermal carbonization [1-3].

2.1. Preparation of Biochar

2.1.1 Pyrolysis

Pyrolysis of biomass has a long history, people have been using pyrolysis to produce charcoal for thousands of years. The traditional kiln pyrolysis not only wastes a lot of resources, but also has poor working conditions and high intensity in the production process, long production cycle, serious pollution and low quality of biochar. In recent years, people have continuously improved the technology and equipment, and developed a new method of biochar pyrolysis. The pyrolysis takes place in oxygen-free conditions at a temperature of between 300 and 1300 °C [2-4]. The initial step is a preprocessing step that usually comprises dewatering, crushing, and screening the raw material. Next, the pyrolysis reaction executes and the products obtained are treated to obtain the final product in a straightforward manner. The pyrolysis process produces three forms of products: solid, liquid and gas. The solids and liquids are commonly known as biochar and bio-oil, while the gases are typically referred to as synthesis gas and contain CO₂, H₂ and NO [3]. Methods of pyrolysis of biochar are categorized according to the heating rate, with pyrolysis being categorized as 'slow', 'fast' and 'flash' pyrolysis. Slow rate pyrolysis is commonly used to produce biochar because it is a slow process with a relatively low heating rate (<5 °C/min), which promotes the pyrolysis of cellulose and other substances (especially lignin), resulting in higher solid and biochar yields, such as torrefaction carbonization. Fast pyrolysis is the process of decomposing biomass into biochar in a fixed, moving or fluidized bed at a rapid heating rate to produce biogas and bio-oil, such as high temperature gasification and microwave pyrolysis technology [8]. The flash pyrolysis process is extremely hot, with a very fast ramp-up rate, and the product is mainly biogas. Table 1 is the characteristics of different pyrolysis methods.

Table 1. Characteristics of different pyrolysis methods.

Factors	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Temperature (K)	350-600	850-1250	1050-300
Heating rate (K/a)	0.1-1.0	10-200	<1000
Size (mm)	5-50	<1	<0.2
Retention time (s)	Mins-hours	1-2	<1

Torrefaction carbonization is a comparatively benign thermochemical process that takes place at temperatures ranging from 200 and 300°C under inert conditions at atmospheric pressure, removing

most of the water and oxygen from the biomass and converting the feedstock into a hydrophobic solid product [9]. The energy density of the biomass can be raised by about 30% by means of roasting. Bridgeman et al. [10] used a multifactorial test method to study the grindability of herbaceous plants (Licorice, wheat straw) and trees (willow branches) at 200~300°C, respectively. The study yielded results indicating that herbaceous biochar had a higher mass loss and lower yield than wood biochar.

Gasification process is carried out using a gasifying agent (air, oxygen, steam, etc.) and consists mainly of steps such as drying, pyrolysis, combustion and mixing. However, the carbon yield is low and toxic by-products are produced. L, used a slow pyrolysis process (400-600 °C) and two fluidized bed systems for low temperature (600-750 °C) gasification.

Microwave thermal cracking is a high-temperature technology that combines thermal decomposition and microwave heating. This has both benefits and drawbacks. It offers the benefits of fast, consistent heating, product stability and ease of production monitoring. Nonetheless, the greatest hindrance to advancing industrial scale production is the high cost of equipment. Therefore, further exploration of its technology is necessary to reduce production costs.

2.1.2 Hydrothermal carbonization

Hydrothermal carbonization is the carbonization of aqueous biomass in a confined space at a lower temperature [10]. The process results in charcoal rich in oxygen-bearing functional groups with high cation exchange capacity (CEC). However, it is mainly dominated by alkane structure with high C/O, which is readily biodegradable and less stable. In addition, the high pressure and large water requirements increase the difficulty of industrialization.

2.2. Characteristics of Biochar

Researching biochar properties can facilitate the identification of its functions and establish a strong foundation for developing distinct modification strategies based on different biochar properties in the future. This can enhance its functions and benefits in environmental remediation and other relevant domains. Biochar is typically alkaline, with carbon, hydrogen, oxygen and nitrogen as the major elements, and its ash contains calcium, magnesium, potassium, sodium and other salt ions that can provide additional adsorption sites for heavy metals, enhance ion exchange and surface complexation, and release soluble ions such as PO_4^{3-} and CO_3^{2-} to form metal precipitates [2, 9]. The main feature of biochar is its pore size, which can be divided into three categories based on pore diameter: macropores, mesopores and micropores. Macropores are larger than 50 nm in diameter, while mesopores range from 2 nm to 50 nm. On the other hand, micropores are less than 2 nm in diameter [1]. Biochar has good adsorption properties due to its pores, and when applied to soil remediation, it can efficiently and rapidly absorb various pollutants in the soil to improve soil quality.

3. Modification Strategies for biochar

Biochar particles are lightweight, small in size and highly alkaline, which limits their ability to extract contaminants from soil and water. Modifying biochar can add active groups to its surface, overcoming the limitations of single biochar particles, improving stability, and creating a high-performance material that increases adsorption potential [3, 8]. Chemical and physical modification are the most popular methods of biochar modification (Fig. 1). Chemical modification includes acid modification, alkaline modification and metal salt or metal oxide modification and has a wide range of applications. Steam modification, gas purging, etc. are the main physical modifications [11].

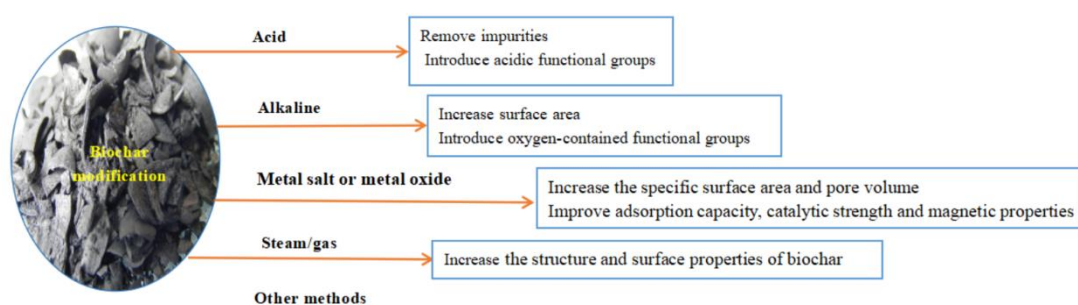


Fig 1. Modification methods of biochar. (Photo/Picture credit: Original)

3.1. Chemical Modification Methods

3.1.1 Alkaline modification method

Potassium hydroxide and sodium hydroxide are frequently used as alkaline agents, which significantly increase specific surface area, the pore volume and surface alkalinity of catalysts, thereby facilitating the adsorption of pollutants [8]. Alkaline modification can change the SSA of biochar, but this metric is also affected by the kind of pyrolysis feedstock and the method of preparation. Biochar extracted from municipal solid waste was modified using sodium hydroxide in a study. The NaOH-modified biochar exhibited an increased SSA and an increase in CEC [12]. In another study, modifying bamboo biochar with sodium hydroxide did not result in an increase in specific surface area [8].

3.1.2 Acid modification method

Acid modification plays an important role in removing minerals and impurities from the pores in the surface of biochar. It achieves this by introducing acid-adsorption sites through the combination of oxygen-containing functional groups such as phenolic groups, carboxyl groups and lactones [8]. Oxidizing agents such as hydrochloric acid, nitric acid, hydrogen peroxide and phosphoric acid are used to activate biochar. As a result of the acid change, biochar exhibits enhanced surface area, increased acidity, and increased polarity.

3.1.3 Metal salt or metal oxide modification method

On the surface of biochar, inorganic substances like metals or metal salts, halogens or their heteroatoms can modify the number, type, and the active sites of functional groups. This modification increases the SSA, porosity and enhances its adsorption capacity, catalytic strength, and magnetic properties. Choi et al. [13] synthesized magnetic banana peel biochar loaded with Fe_3O_4 and used it to remove radioactive Sr from aqueous solution. and used it to remove radioactive Sr from aqueous solution.

3.2. Physical Modification Methods

Physical predominantly include steam modification and gas purging, which are low-cost and easy-to-use activation methods in comparison to other methods. Furthermore, they do not involve the use of any chemical substances. The process is low cost and easy to perform compared to other activation methods, and does not use any chemical substances.

3.2.1 Steam modification method

Steam conversion of biochar both promotes salt removal and crystallized carbon formation, and removes incomplete combustion products generated during initial pyrolysis. Additionally, the steam modification process enhances the structural integrity and surface properties of biochar. The process of steam gasification entails a sequence of reactions between team and biochar, as well as the intermediates of the biochar steam gasification process (equations (1) to (3)) [8]. These reactions lead

to depletion of reaction sites on the surface of biochar, formation of new pores, enlargement and enlargement of pores, and activation of biochar.



3.2.2 Gas purging modification method

Gas purging modification mainly changes the structure and properties of biochar. There are two processes involved in the significant increase of porosity and specific surface area of biochar after modification. One method is utilizing a pyrolysis reaction of the feedstock. Another approach involves modifying the biochar by purifying it using carbon dioxide and/or ammonia. Studies have shown that modifying biochar from wheat stalks with a combination of carbon dioxide and ammonia significantly increases its surface area compared to modifying it with either carbon dioxide or ammonia alone [3].

3.3. Other Modification Methods

Biochar synthesis is an option with more potential for development, as these methods are not limited by the functional groups that can be introduced by chemicals and the biochar surfaces that can be used for doping. There are a number of composite materials, such as magnetic iron oxides (e.g. Fe_3O_4), nanometal oxide / hydroxide (e.g. ZnO) and functional materials (e.g. graphene), that can be used to prepare modified biochar for application-promoting purposes [3, 8, 13].

4. Application of modified biochar in soil remediation

4.1. Enhanced Soil Physical and Chemical Properties

Biochar and modified biochar have the potential to enhance the physicochemical properties of soil, such as increasing soil porosity for better water and nutrient retention as well as raising the CEC and pH levels, in addition to improving the organic carbon content. Biochar is alkaline, because the mineral elements (Ca, K, Mg) in biomass raw materials will form a large number of carbonate, bicarbonate and silicate during the pyrolysis of biochar, which can be combined with H^+ in the soil environment, and thus increase the pH value of the soil. The aromatic hydrocarbon functional groups on the biochar surface can also adsorb H^+ in the soil solution, raising soil pH. The study employed fungal breakdown (FB), bacterial digestion (BB), and iron modification of biochar ($\text{NH}_3\text{-H}_2\text{O-FeCl}_3$) to modify biochar, respectively [12]. The modified biochars showed a significant increase in ash content, SSA and other indicators. The results indicate that biomass modification of FB and BB has significantly enhanced the cadmium adsorption capacity of the resulting biochar when compared to the unmodified biochar. The cadmium adsorption capacity of the unmodified control was 14.8 mg/g. By contrast, the biochar produced from FB yielded a capacity of 36.4 mg/g and the biochar produced from BB yielded a capacity of 30.2 mg/g.

4.2. Treatment of Soil Contaminants

Soil pollution is a significant issue that has a severe impact on the quality of soil environment and human health. Organic pollutants, such as halogenated hydrocarbons like polycyclic aromatic hydrocarbons (PAHs) and antibiotics. Additionally, inorganic substances like trace metals are also present. Biochar mainly adsorbs or passivates heavy metals in soil through redox reaction, surface adsorption, complexation, precipitation, ion exchange and electrostatic effect. The mechanism of organic pollutants is related to the material composition and surface functional groups, including pore filling, surface complexation, ion exchange, electrostatic attraction, hydrogen bonding and redox. Biochar adsorption mechanisms for heavy metals, organic and inorganic contaminants are shown in Fig. 2.

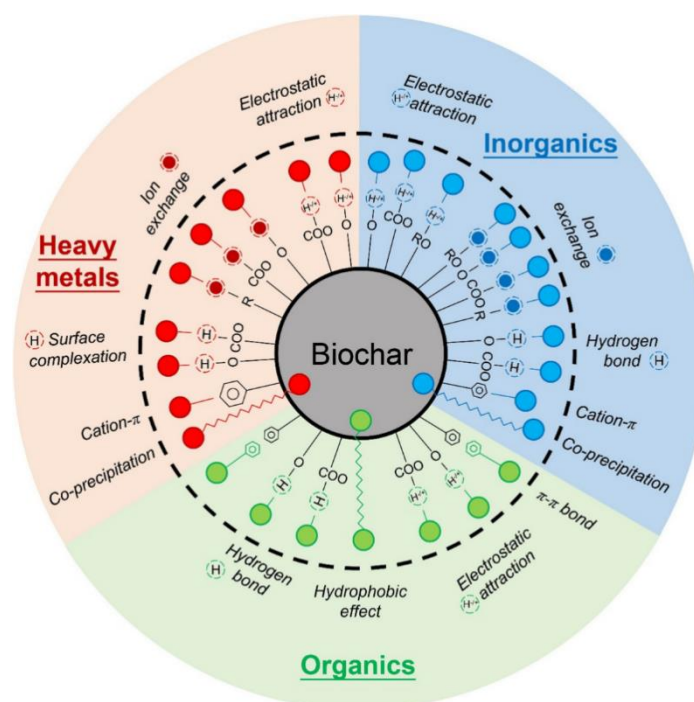


Fig 2. Biochar adsorption mechanisms. <https://doi.org/10.1016/j.scitotenv.2020.142104>.

In terms of adsorption of organic pollutants, a study showed that biochar from mangrove plant residues had a strong adsorption capacity for polycyclic aromatic hydrocarbons (PAHs) in soil and was able to reduce the use of PAHs by plant tissues [9]. The study revealed that the addition of biochar significantly increased the number of soil microorganisms and soil enzyme activity, as well as the soil organic matter content. This improvement in soil properties led to enhanced biodegradation of PAHs. Meanwhile, Wang et al. [14] found the influence of hematite-modified biochar prepared at 600 °C on the removal of heavy metal As(V) in soil and found that the maximum adsorption amount of heavy metal As(V) reached 429 mg kg⁻¹ due to the electrostatic adsorption of modified biochar and the role of surface functional groups, which is about twice that of modified biochar. In conclusion, modified biochar can not only adsorb nutrients and improve soil environmental conditions but also reduce the bioefficacy of harmful elements, thus maximising the benefits of material and energy cycles. The modified biochar can not only improve the environmental conditions of the soil but also reduce the bioeffectiveness of harmful elements, thus maximising the benefits of material and energy circulation, and its results are good for soil improvement. The research on the application of biochar and modified biochar to soil improvement has been relatively in-depth and the effect is remarkable. been more in-depth, and the effect is remarkable.

5. Conclusion

Biochar is not only simple and inexpensive to prepare, but also has a strong adsorption capacity and high activity, and is widely used in environmental remediation. However, traditional biochar has many limitations and needs to be modified for better environmental benefits. Therefore, mass production and batch modification of biochar is particularly important. Modified biochar is a significant material with adsorption capabilities, and its adsorption performance is highly dependent on its SSA and porosity. Moreover, the adsorption performance of modified biochar is closely associated with the number of its functional groups, with an improvement in adsorption performance frequently being accompanied by a higher number of functional groups. Introducing varied functional groups onto modified biochar surfaces can provide specific affinity and selectivity, allowing for effective adsorption of particular pollutants. Modified biochar holds a vast range of potential applications in the areas of water pollutant removal, soil remediation, and soil improvement. It is of great importance for environmental protection and sustainable development. In order to further

advance the research and practice of biochar, it is important to focus on the systematic classification and organization of biochar and its modification processes, and to continue to develop the theoretical framework of biochar. Consideration should be given to the long-term attentions of biochar utilization and application on the environment and its potential to cause secondary pollution. Further summaries of industrial production, engineering applications and standardized control of well-performing biochar are also needed.

References

- [1] Kathrin W., Peter Q., Properties of biochar. *Fuel*, 2018, 217: 240-261.
- [2] Liu Q., Bai G., Research progress of biochar and its modification technology for remediation of soil heavy metal pollution. 2022, 51(11): 3285–3299. (In Chinese)
- [3] Wang J., Wang S., Preparation, modification and environmental application of biochar: A review. *Journal of Cleaner Production*, 2019, 227: 1002-1022. (In Chinese)
- [4] Pan X., Gu Z., Chen W., Li Q., Preparation of biochar and biochar composites and their application in a Fenton-like process for wastewater decontamination: A review. *Science of the Total Environment*, 2021, 754: 142104.
- [5] Zhang X., Miao X., Wei X., et al. Ball milling biochar with ammonia hydroxide or hydrogen peroxide enhances its adsorption of phenyl volatile organic compounds (VOCs). *Journal of Hazardous materials*, 2021, 403: 123540.
- [6] Zhao N., Zhao C., Lv Y., et al., Adsorption and coadsorption mechanisms of Cr(VI) and organic contaminants on H₃PO₄ treated biochar. *Chemosphere*, 2017, 186: 422-429.
- [7] Duca G., Ciobanu M., Lupascu T., et al. Adsorption of Strontium Ions from Aqueous Solutions on Nut Shells Activated Carbons. *Chemistry Journal of Moldova*, 2018, 13(2): 69-73.
- [8] Xie Y., Wang L., Li H., et al., A critical review on production, modification and utilization of biochar. *Journal of Analytical and Applied Pyrolysis*, 2022, 161: 105405.
- [9] Luo P., Wei L., Wang H., Hu Q., Advances in application research of biochar in soil remediation. *Proceedings of the 2022 Annual Scientific and Technical Conference of the Chinese Society of Environmental Science-Environmental Engineering Technology Innovation and Application Session (II)*. 2022, 352-359. (In Chinese)
- [10] Bridgeman T.G., Jones J.M., Shield I., Williams P.T., Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. *Fuel*, 2008, 87: 844-856.
- [11] Rajapaksha, Anushka U., et al., Engineered/designer biochar for contaminant removal/immobilization from soil and water: Potential and implication of biochar modification. *Chemosphere*, 2016, 1: 276-291.
- [12] Xu Y., Wu S., Huang F., Huang H., Yi Z., and Shuai Xue. Biomodification of Feedstock for Quality-Improved Biochar: A Green Method to Enhance the Cd Sorption Capacity of *Miscanthus lutarioriparius*-Derived Biochar. *Journal of Cleaner Production*, 2022, 350: 131241.
- [13] Choi J.W., Cho S., Choi S.J., Ecofriendly, selective removal of radioactive strontium ions in aqueous solutions using magnetic banana peels. *Sci. Total Environ.*, 2021, 778: 146327.
- [14] Wang S., Gao B., Zimmerman A.R., et al., Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite. *Bioresource Technology*, 2015, 175: 391-395.