Modified Biochar: Increasing Adsorption Capacity and its Effects on Soil Pollution

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Abstract: Soil pollution poses significant risks to ecosystems and human health through the spread of heavy metals, organic pollutants, and harmful substances related to agricultural products. The aim of this review is to analyze the current state of biochar use in soil remediation, to reveal its effects on the transport and bioavailability of heavy metals and organic pollutants, and to identify areas for future direction. Biochar has been shown to have the potential to reduce the mobility of pollutants due to its high solid exchange capacity, microporous structure, and functional group density. Modifications can significantly increase surface area and adsorption capacity; this plays a critical role in reducing the bioavailability of heavy metals and organic pollutants. The literature indicates that modified biochar has high application potential due to its low cost and wide accessibility.

Key-Words: Soil, Adsorption, Agricultural, Biochar, Modifications, Adsorption.

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1. Introduction

Industrial pollutants, pesticide and herbicide use, agricultural fertilizers, and fossil fuel consumption have become a significant global problem, posing important risks to soil security and human health [9]. Soil pollutants can generally be classified into two groups: heavy metals and organic compounds. These harmful substances not only negatively affect crop yield and quality but also lead to a decline in air and water quality [11]. Scientists have increasingly begun to examine the use of biochar as a practical solution to minimize soil pollution [18]. It not only improves soil quality physically, chemically, and biologically but also demonstrates high efficiency in pollutant removal. Due to its low cost, abundant availability, and chemical/biological stability, it has recently attracted increasing attention [19]. A study demonstrates the potential of biochar in pollutant removal, showing that it can remove up to 80% of heavy metals from contaminated soils. Biochar synthesized via pyrolysis is an effective material in reducing the mobility and bioavailability of pollutants in soil due to its high cation exchange capacity, large specific surface area, and richness in functional groups [20]. These properties can be further improved by modifying the structure of biochar [21]. The aim of this review is to analyse the current state of research on the role of biochar in soil remediation; to reveal its effects on the transport and bioavailability of heavy metals and organic pollutants; and to shed light on the areas that biochar-focused soil remediation approaches should direct in the future [22].

The modification of biochar can enhance surface chemistry by increasing the density of oxygen-containing functional groups, expand micropore volume to improve adsorption capacity, and enhance structural stability. Modification strategies are generally classified into three main categories: chemical modification, physical modification, and biological modification. In recent years, the growing interest in biochar and related carbon materials within the scientific community has contributed to a marked increase in studies and

academic publications focused on modified biochar [6].

2. Biochar Feedstock Sources

Feedstock Sources

Features of Biochar depends on combination and structure of biomass which is used for production.It is considered that biomass is divided into two main catagories in general, one is called lignocellulosic and the other one is non-lignocellulosic.

To give an concrede examples about lignocellulosic biomass, these are ;

1) Woody materials
2) Agricultural wastes
3) Plant stems
4) Forestral wastes and shells

These biomasses explained above contain high amount of carbon and generate determined biochar while pyrolysis

To give an concrede examples about non-lignocellulosic biomass, these are ;

1) Algaes
2) Food wastes
3) Animal fertilizers
4) Sewage muds

These biomasses explained above contain high amount of ash and nitrogen. This situation increases the reactivity but decreases the efficiency.

Main elements of biochar and their corruption temperatures.

1) Cellulose 220–315 °C
2) Hemicellulose 315–400 °C
3) Lignin 200–500 °C
4) Extractives (a few amount)

For this reason wealth feedstock in terms of lignin provides high carbon efficiency and to occur more stable biochar. [1]

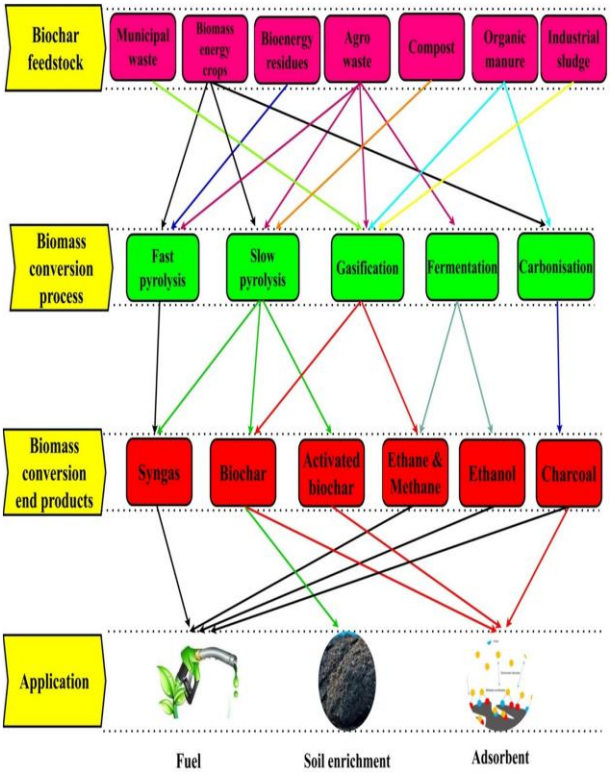


Fig. 1 The overall conversion process of biomass into biochar and its application. [1]

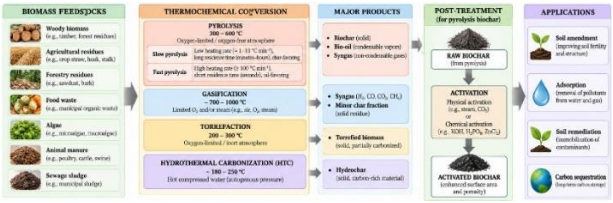


Figure 2. Biomass-to-biochar conversion pathways, representative process conditions, major products, and post-treatment options [1]. Note: Process conditions are representative ranges. Actual values may vary depending on feedstock characteristics, reactor configuration, heating rate, residence time and reaction atmosphere.

The properties of biochar depend strongly on the composition, structure, and origin of the biomass used as feedstock. Biomass feedstocks used for biochar production can generally be classified into lignocellulosic and non-lignocellulosic materials.

Typical lignocellulosic feedstocks include woody biomass, agricultural residues, plant stems, forestry residues, and shells. These materials generally contain relatively high proportions of carbon and

lignocellulosic components and are widely used for biochar production through pyrolysis.

Non-lignocellulosic feedstocks include algae, food waste, animal manure, and sewage sludge. Compared with many lignocellulosic feedstocks, these materials may contain higher proportions of ash, nitrogen, and inorganic constituents, which can significantly influence the yield and physicochemical properties of the resulting carbonaceous products.

The major structural components of lignocellulosic biomass undergo thermal decomposition over different temperature ranges. Cellulose generally decomposes at approximately 220–315 °C, hemicellulose at approximately 315–400 °C, and lignin over a broader range of approximately 200–500 °C. Feedstocks with relatively high lignin contents generally tend to favor the formation of carbon-rich and thermally stable solid products.

The major biomass feedstocks and thermochemical conversion pathways relevant to biochar and related carbonaceous products are summarized in Figure 1.

3. Biochar Production Methods and Process Mechanisms

General Perspective Of Biochar Production Technologies.

Production of biochar basically depends on thermochemical conversion of biomass.In this period, on some conditions that oxygen is limited or utterly extinct , is obtained wealth carbon solid product (biochar), liquid phase (bio-oil) and gas phase (syngas) by heating biomass.

Major technologies used in producing biochar.

1) Pyrolysis
2) Gasification
3) Torrefaction
4) Hydrothermal Carbonization is classified as.

Each of these methods show some differences in terms of temperature, pressure, residence time, heating speed and atmosphere conditions. As a result of that the properties of biochar that occurred are also different. [2]

Biochar and related carbonaceous materials can be produced from biomass through several thermochemical conversion pathways. Among these technologies, pyrolysis is the principal route for the production of conventional biochar and generally produces three major product fractions: a solid carbon-rich fraction (biochar), condensable vapors (bio-oil), and non-condensable gases (syngas).

Other thermochemical processes produce different types of carbonaceous products. Gasification is primarily designed for syngas production and may generate a relatively small amount of char as a solid residue. Torrefaction is a mild thermal treatment that produces a partially carbonized solid known as torrefied biomass. Hydrothermal carbonization (HTC), in contrast, is particularly suitable for wet biomass and produces a carbon-rich solid known as hydrochar.

The operating conditions of these processes, including temperature, heating rate, residence time, pressure, and reaction atmosphere, strongly influence product distribution and the physicochemical characteristics of the resulting carbonaceous materials. The major conversion pathways and representative operating conditions are presented in Figure 2.

3.1. Pyrolysis

Pyrolysis is a disintegration of biomass as a thermal. The basic reaction executes in nonoxygen place and three main products are generated.

1. Biochar
2. Bio-oil
3. Syngas

Duration of pyrolysis: This process is classified in three different way depends on the temperature, heating speed, residence time and feedstock features.

- Slow pyrolysis: Even though the low heating speed (5–10 °C/minute) and the long residence time (5–10 °C/minute), this method offers the highest biochar efficiency.
- Fast pyrolysis: Thanks to the high heating speed and short residence time, more bio-oil is produced but this process reduces the rate of biochar.
- Flash pyrolysis: In this process, high temperature is applied in rather short time. Thus, biochar is obtained with its nanoporous and reactive surface.

When the pyrolysis temperature gradually rises, the carbon content increase, the oxygen/hydrogen rate decreases and the functional groups that are on the surface decrease. This situation increases the chemical stability of biochar, but it may weaken its interaction with polar pollutants. [1]

Pyrolysis is a thermochemical conversion process in which biomass is heated under oxygen-limited or oxygen-free conditions. Depending on the operating conditions, pyrolysis produces three major product fractions: biochar, bio-oil, and syngas. The relative proportions of these products depend mainly on temperature, heating rate, residence time, feedstock characteristics, and reactor configuration.

Pyrolysis can be broadly classified into slow, fast, and flash pyrolysis according to the heating rate, residence time, and operating conditions.

- **Slow pyrolysis:** Slow pyrolysis is characterized by a relatively low heating rate and a long residence time. Typical heating rates are approximately 0.1–1 °C s^{-1} (6–60 °C min^{-1}), although lower rates are also reported depending on reactor design and feedstock. Longer residence times favor the formation of solid carbonaceous products and generally increase the relative biochar yield.
- **Fast pyrolysis:** Fast pyrolysis is characterized by a high heating rate and a short residence time, generally favoring the formation of bio-oil. The process commonly operates at approximately 450–600 °C with vapor residence times of only a few seconds.
- **Flash pyrolysis:** Flash pyrolysis employs extremely high heating rates and very short residence times. Under these conditions, rapid volatilization occurs and the process generally favors liquid and gaseous products, while the biochar fraction is relatively low.

In general, increasing pyrolysis temperature promotes devolatilization and carbonization, resulting in higher carbon content and lower hydrogen and oxygen contents. Increasing temperature may also reduce the abundance of some oxygen-containing surface functional groups and increase the aromatic character and thermal stability of biochar. However, the magnitude and direction of these changes depend on feedstock composition and other process parameters.

3.2. Gasification

Gasification is a process and in this process biomass is converted with limited oxygen or steam exist between 700–1000 °C by using particially oxidation. Main product is syngas which usually includes CO, H_2 CO_2 CH_4. Biochar which is generated as a axiulary product, even if there is less amount, because of the high surface area and graphitic structure is able to us efor energy storage and electrochemical application.

Advantages of Gasification :

- It provides energy recovery
- It decreases CO_2 emission
- It produces a gas phase product which can be used as a fuel.

Even though this process has some advantages, it has a disadvantage that is low eficiency of biochar. For this reason, gasification usually focus on the fuel production. [2]

Gasification is a thermochemical conversion process in which biomass is converted under high-temperature conditions in the presence of a limited amount of oxygen and/or steam. The process generally operates at approximately 700–1000 °C and involves partial oxidation of the feedstock. The main product is syngas, which typically contains CO, H_2, CO_2, and CH_4.

A relatively small amount of carbonaceous solid residue or char may also be generated during gasification. Because gasification is primarily designed to maximize gaseous products, its biochar yield is generally much lower than that of slow pyrolysis. Therefore, gasification is mainly employed for energy recovery and syngas production rather than for maximizing biochar production.

The main advantages of gasification include energy recovery, production of a combustible gas product, and efficient conversion of biomass into useful gaseous fuels. However, the relatively low

yield of solid carbonaceous material limits its use when the primary objective is biochar production.

3.3. Torrefaction

Torrefaction is a mild pyrolysis process and in this process biomass is heated between 200-300 °C in nonoxygen atmosphere. The reason is that in this process; increase the energy intensity of biomass decrease the moisture content and maket he biochar more stable. While this process, whereas lignin partially creates aromatic carbon structure, hemicellulose is highly disintegrated. As a result, torrefied biochar obtanied may combine with coal foe energy production or may use with a view to capturing carbon. Torrefaction is preferred so as to make the low intensity biomasses such as agriculture wastes wealth in terms of energy. [2]

Torrefaction is a mild thermochemical treatment of biomass generally performed at approximately 200–300 °C under an oxygen-limited or inert atmosphere. The process removes moisture and a portion of the volatile components while increasing the energy density, hydrophobicity, and grindability of the biomass.

Unlike conventional pyrolysis, torrefaction is primarily considered a biomass pretreatment or mild carbonization process rather than a conventional biochar production route. The main solid product is therefore referred to as torrefied biomass. During torrefaction, hemicellulose undergoes substantial thermal degradation, while part of the lignin structure is retained and transformed into a more aromatic carbonaceous structure.

Torrefied biomass can be used as a solid fuel, blended with coal, or further processed for other energy and material applications. The final characteristics of the torrefied product depend on feedstock composition, treatment temperature, residence time, and heating rate.

3.4. Hydrothermal Carbonization – HTC

HTC is the best appropriate medhods for feedstocks that have high humidity rate. (For instance, food wastes, algaes, sewage muds). In this process, biomass is run for a few hours under 2-5 Mpa, between 180-250 °C temperature in closed reactor with water. At this period water shows supercritical features and some reactions actualize such as hydrolysis, dehydration, condensation and polymerization which of them ease the disintegrate of biomass. The last product is hydrochar which has high carbon rate.

The Advanteges of HTC:

- The pre-drying does not require. (Humidity biomass can able to use directly.)
- High carbon efficiency (% 60-80)
- Short transaction time
- Efficient transformation in terms of energy

Therefore, HTC plays a significant key role producing sustainable biomass within the scope of cicular economy. [2]

Hydrothermal carbonization (HTC) is particularly suitable for biomass feedstocks with high moisture content, such as food waste, algae, and sewage sludge. Unlike conventional pyrolysis, HTC does not require extensive pre-drying of the feedstock because water serves as the reaction medium.

HTC is generally conducted in a closed reactor at approximately 180–250 °C under autogenous pressure generated by the heated water. Under these subcritical hydrothermal conditions, reactions such as hydrolysis, dehydration, decarboxylation, condensation, and polymerization contribute to the conversion of biomass into a carbon-rich solid **carbonaceous products [2].** product known as hydrochar.

The main advantages of HTC include the ability to process wet biomass without intensive pre-drying, relatively efficient carbon conversion, and the production of a carbon-rich solid product. The properties and yield of hydrochar depend on

Conversion method	**Representative operating conditions**	**Main product(s) and characteristics**	**Typical yield / range**	**Main applications**
Pyrolysis	**300–600 °C**; oxygen-limited or oxygen-free atmosphere; residence time from minutes to hours depending on process type	**Biochar** (solid), **bio-oil** (condensable liquid), and **syngas** (non-condensable gases). Slow pyrolysis generally favors the solid fraction and produces carbon-rich, aromatic biochar.	Biochar typically **~25–50 wt.%** in slow pyrolysis; product distribution depends strongly on temperature, heating rate, residence time, and feedstock	Soil amendment, contaminant adsorption, soil remediation, carbon sequestration, and production of activated biochar
Gasification	**~700–1000 °C**; limited O_2 and/or steam; typically short residence times of **seconds to minutes**	**Syngas** is the principal product, mainly containing CO, H_2, CO_2, and CH_4; a relatively small amount of char residue is also produced	Char/solid fraction generally **<10–12 wt.%**; syngas may account for **~80–90 wt.%** of the product gas fraction depending on conditions	Syngas production, energy recovery, heat and power generation; char residue may be further used in adsorption or electrochemical applications
Torrefaction	**200–300 °C**; oxygen-limited or inert atmosphere; typically **10–60 min**, although longer residence times may be used depending on reactor and feedstock	**Torrefied biomass**, a partially carbonized, hydrophobic, energy-dense solid with improved grindability and reduced moisture content	Solid yield typically **~60–90 wt.%**	Solid fuel, co-firing with coal, biomass densification, and as a pretreatment for subsequent thermochemical conversion
Hydrothermal carbonization (HTC)	**~180–250 °C**; hot compressed water in a closed reactor; autogenous pressure typically in the **MPa range**; residence time generally **1–16 h**	**Hydrochar**, a carbon-rich solid produced from wet biomass; hydrolysis, dehydration, decarboxylation, condensation, and polymerization contribute to its formation	Hydrochar typically **~50–80 wt.%** depending on feedstock and operating conditions	Carbon-rich material production, soil amendment, adsorption, energy applications, and carbon management; particularly suitable for wet biomass

Table 1. Comparison of major thermochemical conversion pathways for biochar and related temperature, residence time, biomass-to-water ratio, feedstock composition, and reaction conditions.

Table 1. Comparison of major thermochemical conversion pathways for biochar and related carbonaceous products [2]. Note: The operating conditions and product yields presented in this table are representative literature ranges rather than universal limits. Actual values vary depending on feedstock composition, reactor configuration, heating rate, residence time, reaction atmosphere, and other process parameters.

4. Physical And Chemical Features Of Biochar

Features of biochar depend on both feedstock species and product parameters.
The main features are as follows:

- Surface area: It is between 50-500 m^2/g. It can reach of >1000m^2/g values by activation
- Pore structure: Micro (<2 nm), Mezo (2–50 nm) ve Macrosurface (>50 nm) rates change depending on the product temperature.
- Surface functional groups: –OH, –COOH, –C=O, $–NH_2$ groups play critical role on polluting adsorption.
- Chemical stability: When the rate of aromatic carbon circles high, biochar gain the resistance againts of the environmental disintegrate.
- Ph and Ash content: The biochars that produces in high temperature exhibits more alkaline character. (Ph>9)

These features directly determine the performance of biochar on environmental applications. [1]
The physicochemical properties of biochar are strongly influenced by feedstock composition and production conditions, particularly pyrolysis temperature, heating rate, residence time, and reaction atmosphere. These properties determine the suitability of biochar for applications such as soil amendment, contaminant adsorption, and environmental remediation.

The major physical properties include particle size, specific surface area, pore size, pore volume, and bulk density. The specific surface area of biochar can vary widely depending on feedstock and thermochemical conditions. Reported values range from very low values to several hundred $m^2\ g^{-1}$, while activation and other post-treatment processes can increase the specific surface area to above 1000 $m^2\ g^{-1}$. Therefore, no single surface-area value can be considered representative of all biochars.

Pore structure is commonly classified according to pore diameter into micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). This hierarchical pore structure plays an important role in mass transfer and adsorption of contaminants.

The main chemical properties include pH, electrical conductivity, surface functional groups, and elemental composition. Biochar commonly exhibits neutral to alkaline characteristics, although reported pH values vary substantially with feedstock and production conditions. Electrical conductivity is similarly dependent on the mineral and soluble salt content of the feedstock and biochar.

Surface functional groups such as hydroxyl (–OH), carboxyl (–COOH), carbonyl (C=O), phenolic, and amino ($–NH_2$) groups contribute to the surface reactivity and adsorption behavior of biochar. These functional groups can be characterized using techniques such as Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

Elemental composition, particularly the relative contents of carbon, hydrogen, oxygen, nitrogen, sulfur, and ash, provides important information about the degree of carbonization and the chemical stability of biochar.

Representative definitions, units, classifications, and literature ranges for the major physicochemical properties are summarized in Figure 3.

PHYSICAL PROPERTIES			
Property	**Definition**	**Unit**	**Representative range / classification**
Particle size	Size or size distribution of biochar particles	mm or µm	Application/post-processing dependent; commonly < 0.063 mr to several mm
Specific surface area (SSA)	Surface area available per unit mass	$m^2\ g^{-1}$	~ 0.1 – 500 (activated biochar can exceed 100
Pore size	Characteristic diameter of pores	nm	Micropores < 2 nm; mesopores 2 – 50 nm; macropores > 50 nm
Bulk density	Mass of biochar per unit bulk volume	$g\ cm^{-3}$	~ 0.05 – 0.70

Figure 3. Major physicochemical properties of biochar, their definitions, units, and representative literature ranges [1].

Note: Reported ranges are representative literature values rather than universal limits. Values may vary depending on feedstock, production temperature, residence time, reactor conditions, post-treatment, and analytical method.

5. Effect of Production Parameters

Structural and chemical features of biochar depends on the variables on production conditions. These features may be affected by the changes that is mentioned above.

1. Temperature :

High Temperature → high carbon rate, low hydrogen/oxygen rate. Nevertheless high temperature causes the loss of functional groups (–OH, –COOH).

2. Residence time:

Long time → more aromatic structure but energy consume may increase.

3. Heating speed:

Low heating speed → high biochar efficiency.

High speed → more gas and liquid product.

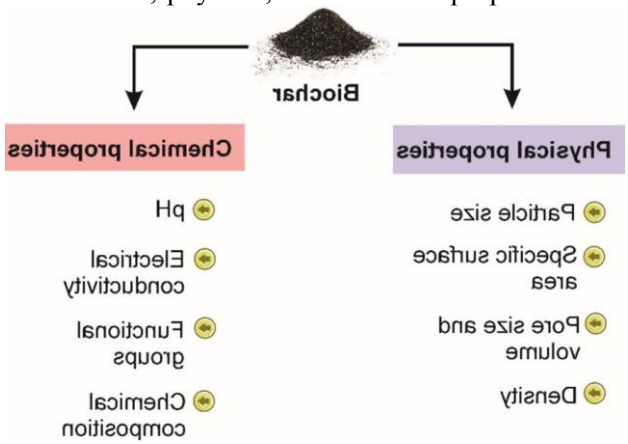
4. Feedstock type :

High Lignin rate feedstock → produces the stable and carbon-rich biochar.

1. Atmosphere conditions :

Nitrogen, argon or vacuum atmosphere prevents the oxidation, hence it reduces the carbon loss. [2]

The structural, physical, and chemical properties of



biochar are strongly influenced by the conditions under which biomass is thermochemically converted. The most important parameters include temperature, residence time, heating rate, feedstock characteristics, and reaction atmosphere.

5.1. Temperature

Increasing the pyrolysis temperature generally promotes devolatilization and carbonization. As a result, the relative carbon content and aromaticity of

Production Method	**Product Name**	**Characteristic Feature**	**Application Area**
Pyrolysis	Biochar	High surface area – aromatic structure	Soil, purification
Gasification	Char residue	Low amount, high purity	Electrochemistry
Torrefaction	Torrefied char	Intense energy, hydrophobic	Fuel additive
HTC	Hydrochar	Suitable for humid foods, high carbon	Carbon storage

biochar generally increase, whereas hydrogen and oxygen contents and some oxygen-containing surface functional groups tend to decrease. Higher temperatures may also enhance pore development and specific surface area, although the magnitude of these changes depends strongly on feedstock characteristics.

5.2. Residence Time

Residence time affects the extent of biomass conversion and secondary reactions. Longer

residence times generally promote further carbonization and aromatization, although excessively long residence times may increase energy consumption and do not necessarily result in higher biochar yields.

5.3. Heating Rate

Heating rate influences the distribution of pyrolysis products. Lower heating rates generally favor solid carbonaceous products, whereas higher heating rates and shorter residence times favor the formation of volatile products and, under fast pyrolysis conditions, bio-oil.

5.4. Feedstock Type

Feedstock composition has a major influence on biochar yield and properties. Feedstocks with relatively high lignin contents generally favor the formation of carbon-rich and more stable solid products, whereas mineral-rich and nitrogen-rich feedstocks may produce biochars with different ash contents, pH values, and surface properties.

5.5. Reaction Atmosphere

The reaction atmosphere affects the extent of oxidation and the final structure of the carbonaceous product. Inert gases such as nitrogen or argon are commonly used to minimize oxidation during pyrolysis. The use of oxygen-limited conditions helps preserve carbon in the solid product and influences the distribution of biochar, bio-oil, and gaseous products.

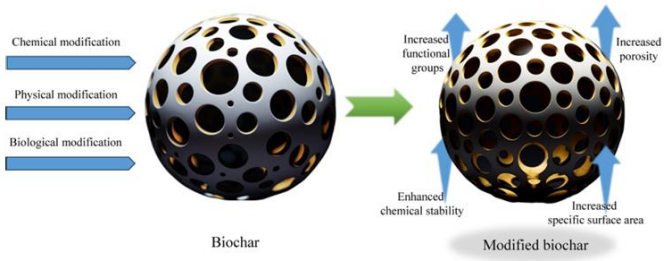
Feature Differences Due To Production.

Table 1. Biochar that is created by every methods, has different structural and functional features [2]

6. Biochar modification methods

Studies on biochar modification have increased significantly in recent years because modification can improve its performance in environmental and agricultural applications. Raw biochar may have limitations related to specific surface area, pore accessibility, and the abundance or accessibility of active functional groups, which can restrict its adsorption performance and other functional uses. To address these limitations, modification strategies are generally classified as physical, chemical, and biological approaches [8]. These approaches differ in their primary mechanisms: physical modification mainly changes particle size and pore structure; chemical modification changes surface chemistry, functional groups, or elemental composition; and biological modification introduces or promotes biological interactions at the biochar surface.

Fig 3. Preparation, Modification Techniques, and



Environmental Applications [8].

The methods employed for the modification of biochar encompass chemical, physical, and biological approaches (Figure 3). As illustrated in Figure 3, these modification routes can produce changes in surface area, pore structure, functional-group abundance, chemical stability, and other material characteristics that influence environmental performance [8].

Figure 4 focuses on the three general modification pathways and their main outcomes. Physical modification is associated primarily with structural and pore development; chemical modification with changes in surface functional groups; and biological modification with biologically mediated changes at the biochar surface. The figure highlights increased functional-group abundance, enhanced porosity, increased specific surface area, and improved

hemical stability as the principal material-level outcomes through which modification can influence adsorption and related environmental functions [6]

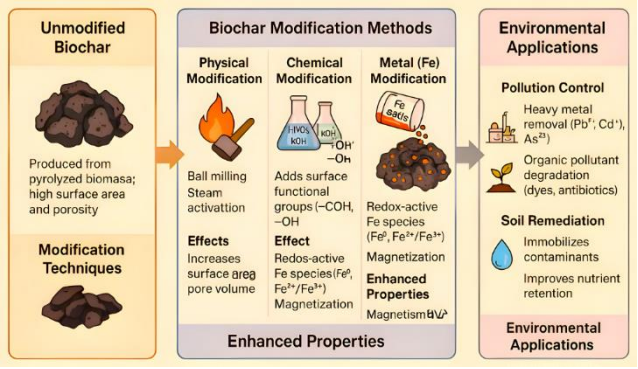


Fig 4. Biochar Modification [6].

6.1. Physical modification

Physical modification methods primarily alter the structure and accessibility of the biochar surface while minimizing the introduction of additional chemical reagents. These methods can increase specific surface area, open or enlarge blocked pores, reduce particle size, and remove impurities that limit access to adsorption sites. Consequently, the principal mechanism of physical modification is structural rather than chemical: changes in pore architecture and surface accessibility can increase the number of sites available for interaction with pollutants. Some physical treatments can also indirectly influence surface chemistry [7].

Physical modification is generally performed after pyrolysis, although the exact sequence depends on the treatment. Steam activation is one example in which superheated steam passes through the pores of biochar at elevated temperature; the cited review reports a temperature range of approximately 650–950 °C [5]. Under such conditions, the pore structure is developed and the accessibility of the internal surface can be increased. This treatment therefore differs from chemical modification because the principal objective is to modify the physical architecture of the material rather than deliberately introduce a new chemical reagent or functional group.

Commonly reported physical modification techniques include ball milling and steam activation, while gasification has also been discussed as a route for altering biochar structure [8]. Ball milling mainly reduces particle size and can expose previously inaccessible surface regions, whereas steam activation develops the pore structure. These mechanisms should therefore be distinguished when interpreting changes in adsorption performance: an observed increase in adsorption may result from greater surface accessibility and pore development rather than from the formation of new chemical binding sites.

6.2. Chemical modification

Chemical modification is one of the most widely used approaches for tailoring the surface chemistry of biochar. It includes acid, alkaline, oxidative, metal-loading, and related treatments. Unlike physical modification, the central mechanism is a change in surface composition and chemical functionality. Acid treatments can introduce or increase acidic oxygen-containing groups and improve porosity; alkaline treatments can alter surface functional groups, specific surface area, and pore volume; and oxidative treatments can increase the abundance of oxygen-containing groups. Metal loading can additionally introduce redox-active sites and metal-associated reaction pathways [8]. These different mechanisms mean that chemical modification should not be treated as a single process with a uniform effect on pollutant adsorption or transformation.

Acid and alkaline treatments can both modify the structure of biochar, but their reported chemical effects differ. Acid treatment can remove mineral residues or impurities and increase the presence of carboxyl groups, which can contribute to cation retention. Alkaline treatment can remove ash and increase hydroxyl-containing surface functionality, thereby favoring interactions with oxyanions. The resulting change in pollutant affinity therefore depends on the type of treatment and on the chemical form of the target pollutant [8].

6.2.1. Heteroatom Doping

Heteroatom doping is a chemical modification approach in which elements such as nitrogen (N), phosphorus (P), sulfur (S), or boron (B) are incorporated into or associated with the carbon structure. The modification changes the electronic

properties and surface chemistry of biochar, thereby creating or altering active sites relevant to adsorption and redox reactions. In this sense, heteroatom doping differs from simple acid or alkaline washing because the modification is associated with a change in elemental composition and electronic structure.

Nitrogen-doped biochar (N-doped biochar): Pyridinic-N and graphitic-N structures can increase electron-transfer capacity and provide reactive surface sites for pollutant-related reactions.

Sulfur-doped biochar (S-doped biochar): Sulfur-containing structures, including S–C–S and C–S–C bonds, can participate in persulfate (PDS) activation and promote the formation of reactive species such as hydroxyl radicals (•OH) and sulfate radicals (SO_4•–).

Boron-doped biochar (B-doped biochar): Boron incorporation can modify the electronic characteristics of the carbon surface and has been associated with the generation of singlet oxygen ($^1O_2$) and the degradation of antibiotics and pesticides [3].

6.2.2. Metal-Loaded Biochar

Metal-loaded biochar is produced by incorporating transition metals such as Fe, Mn, Co, Cu, or Zn into or onto the biochar matrix. The key difference from heteroatom doping is that the modification introduces metal-associated active sites and, in some systems, redox couples that can participate directly in catalytic reactions. These modifications can enhance radical-generation pathways and thereby improve pollutant transformation or adsorption [8].

Fe-loaded biochar: Fe-containing sites can participate in Fenton-type and persulfate-activation reactions. The Fe^{2+}/Fe^{3+} redox cycle can facilitate the generation of reactive species such as hydroxyl radicals (•OH) and sulfate radicals (SO_4•–).

Zero-valent iron-supported biochar (ZVI/BC): Surface –COOH and –OH groups can mediate interactions and electron transfer involving Fe^0 and support persulfate activation. This type of composite has been reported for the degradation of persistent organic pollutants such as atrazine and tetrachlorophenol.

Bimetallic biochar: In systems such as Fe–Mn, interactions between the two metals can facilitate electron transfer and the re-reduction of metal ions. Such redox behavior has been associated with improved performance in antibiotic removal and heavy-metal adsorption [3].

6.2.3. Biochar Composites

Composite biochars are multifunctional materials obtained by combining biochar with polymers, minerals, or nanomaterials. Their modification mechanism depends on the incorporated component: polymers can mainly improve mechanical and water-retention properties; mineral phases can provide additional ion-binding or nutrient-related functions; and magnetic or metal-containing components can add recoverability or redox activity. Therefore, the environmental performance of a composite should be interpreted in relation to the specific component introduced rather than attributed to biochar modification in general.

Biochar–polymer composites: These composites can improve mechanical strength and water-retention capacity, which may support the physical stability and handling of the material in environmental applications.

Biochar–mineral composites: Combinations with phosphorus- or calcium-based minerals can modify nutrient-release behavior and provide additional mineral phases that may interact with contaminants or nutrients in soil [3].

Magnetic biochar: Incorporation of magnetic components such as Fe_3O_4 or MnO_2 can provide magnetic recoverability and may improve functional stability across a range of pH conditions. These properties are particularly relevant to water-treatment applications, where recovery of the modified material can be advantageous [3].

6.3. Biological modification

Biological modification uses biological agents, such as microorganisms or plants, to alter the surface environment and functional behavior of biochar. Unlike physical modification, which

primarily changes structure, and chemical modification, which primarily changes surface chemistry or composition, biological modification depends on biological colonization, growth, and biodegradation processes. Microorganisms can be introduced onto the biochar surface and cultivated in situ, allowing the biochar to act as a support for biological activity [8].

One approach is to inoculate microorganisms into the pores of biochar and allow them to proliferate under suitable conditions. The biochar can provide a porous support for bacteria, fungi, or algae, while the microorganisms contribute biodegradation activity. The cited literature describes this approach mainly for organic-pollutant removal in aquatic systems, including the degradation of lipophilic compounds such as PHAs, DDT-related compounds, and PAHs [6]. Therefore, these results should be interpreted as evidence of biological treatment potential rather than as direct proof of field-scale soil remediation.

Overall, the three modification routes act through different but potentially complementary mechanisms. Physical modification mainly increases accessibility through changes in particle size and pore structure; chemical modification changes surface functional groups, elemental composition, or redox-active sites; and biological modification introduces or supports biological activity on the biochar surface. The resulting changes in adsorption or pollutant transformation should therefore be evaluated together with the relevant material properties and experimental conditions. In particular, increased adsorption capacity should not automatically be interpreted as pollutant removal or immobilization, because these outcomes represent different environmental processes. The distinction is important when comparing modified biochars across studies [3].

7. Application of Biochar in Soil Remediation

7.1. Removal of Heavy Metals

Biochar is used in heavy-metal-contaminated soils primarily as an immobilizing amendment rather than as a material that destroys or permanently removes metals from the soil matrix. Its effectiveness arises from the conversion of dissolved and exchangeable metal species into less mobile, less bioavailable forms through a combination of physical sorption and chemical reactions. The relative importance of these processes depends on biochar feedstock, pyrolysis conditions, surface chemistry, mineral content, soil pH, competing ions, and aging after soil application [20].

The principal mechanisms illustrated in Figure 5 are physical sorption, electrostatic interaction, surface complexation, ion exchange, surface precipitation, and metal–π interaction. Physical sorption occurs when metal species are retained within micro- and mesopores or on accessible external surfaces through non-specific surface forces; this contribution generally increases with pore accessibility and specific surface area. Electrostatic interaction is controlled by the charge of the biochar surface and the speciation of the metal. At soil pH values where oxygen-containing groups are deprotonated, negatively charged sites can attract positively charged metal ions. Surface complexation is more specific: carboxyl, hydroxyl, phenolic, carbonyl, and related functional groups can coordinate metal ions and form relatively stable inner- or outer-sphere surface complexes [20].

Ion exchange involves the replacement of exchangeable cations associated with biochar, such as Ca2+, Mg2+, K+, or Na+, by contaminant metal ions. Surface precipitation occurs when metals react with carbonate-, phosphate-, hydroxide-, or other mineral-bearing phases associated with biochar and form sparingly soluble solids; the alkaline character of many biochars can further favor these reactions by increasing soil pH. Metal–π interactions arise from the attraction of metal ions to π-electron-rich aromatic domains within the carbon matrix. These mechanisms are not mutually exclusive and may operate simultaneously. Modification can shift their relative importance; for example, sulfur functionalization can improve Hg immobilization, while mineral- or metal-loaded biochars can introduce additional complexation, precipitation, and redox-active sites [17].

Note: The mechanisms listed above commonly occur simultaneously. Their relative contribution varies with feedstock, production conditions, modification method, soil chemistry, contaminant speciation, and aging. Table adapted conceptually from [20] and [19].

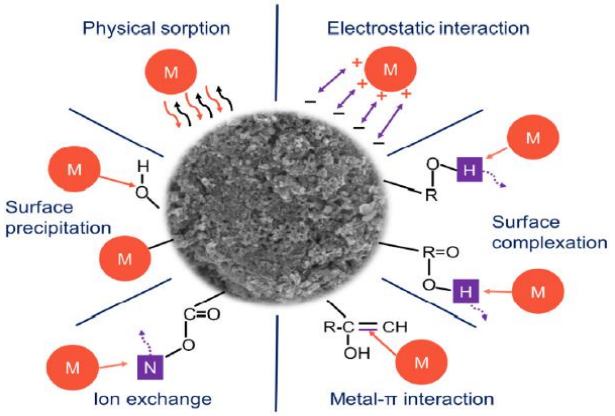


Fig. 5. Major mechanism through which biochar stabilizes heavy metals in soil [22].

Table 2. Major mechanisms by which biochar immobilizes heavy metals in soil.

Mechanism	Physicochemical basis	Biochar features involved	Expected stabilization effect	Representative support
Physical sorption	Retention on external surfaces and within micro-/mesopores through non-specific surface forces and pore filling.	Accessible pore network; specific surface area; pore volume.	Lowers dissolved metal concentration and limits short-range mobility.	[20]
Electrostatic interaction	Attraction between charged surface sites and ionic metal species; strongly dependent on pH and metal speciation.	Deprotonated oxygen-containing groups and overall surface charge.	Promotes retention of cationic metals on negatively charged surfaces.	[20]
Surface complexation	Coordination of metal ions with surface functional groups, forming inner- or outer-sphere complexes.	–COOH, –OH, phenolic, carbonyl and related functional groups.	Converts labile metal species into more strongly surface-bound forms.	[20]
Ion exchange	Exchange of contaminant metal ions with Ca2+, Mg2+, K+, Na+ or other exchangeable cations on biochar.	Cation-exchange sites; oxygen-containing groups; mineral fraction.	Reduces exchangeable and plant-available metal fractions.	[20]
Surface precipitation	Formation of sparingly soluble metal carbonates, phosphates, hydroxides or mineral-associated precipitates.	Ash/mineral constituents; carbonate/phosphate phases; alkaline pH.	Transfers metals into relatively stable solid phases with lower solubility.	[20]
Metal–π interaction	Interaction of metal ions with π-electron-rich aromatic domains in the carbon matrix.	Aromatic and graphitic carbon structures.	Provides an additional adsorption pathway that can complement complexation and ion exchange.	[19]

Figure 5 integrates these pathways around the biochar particle. The upper-left sector represents physical sorption, the upper-right sector electrostatic interaction, the right sector surface complexation, the lower-right sector metal–π interaction, the lower-left sector ion exchange, and the left sector surface precipitation. Together, these processes explain why biochar can decrease the soluble and plant-available fractions of metals even when the total concentration of the metal in soil is not substantially changed. Accordingly, the figure should be interpreted as a mechanistic representation of immobilization rather than chemical destruction of heavy metals [20].

Experimental studies are consistent with these immobilization mechanisms. In Cu-contaminated soil, application of 5% chicken-manure-derived biochar decreased Cu uptake by Oenothera picensis from 66.9 to 36.6 mg kg−1, corresponding to an approximately 45% reduction in plant uptake [10]. Sulfur-modified rice-husk biochar was effective in the remediation of Hg-contaminated soil, illustrating how targeted surface functionalization can strengthen metal-specific stabilization (O'Connor et al., 2018). Rice-husk and wheat-straw biochars also reduced Hg accumulation in rice, with rice-husk biochar showing the stronger effect in the reported study [12].

Sewage-sludge biochar produced at 600 °C was reported to reduce methylmercury (MeHg) and

total Hg (THg) accumulation in rice by 73.4% and 81.9%, respectively, under the conditions evaluated by Zhang et al. (2019). Similarly, plant-derived biochars applied at 2% and 4% reduced the availability and plant uptake of several metals; the 4% Casuarina-derived biochar treatment was among the most effective for metals including Cd, Cu, Ni, and Pb [18]. Collectively, these studies indicate that biochar can decrease mobile and bioavailable metal fractions and reduce transfer to plants. However, performance should be evaluated over longer periods because aging, changes in pH and redox conditions, competition with dissolved organic matter and other ions, and possible desorption can alter immobilization efficiency over time [20].

7.2. Adsorption and Reduced Bioavailability of Organic Pollutants

Biochar can reduce the mobility and bioavailability of a broad range of organic contaminants, including pesticides, steroid hormones, polycyclic aromatic hydrocarbons (PAHs), and some pharmaceutical residues. In contrast to heavy metals, organic contaminants may be retained by partitioning into non-carbonized domains, pore filling, hydrophobic interactions, π–π interactions with aromatic carbon, hydrogen bonding, and electrostatic interactions with surface functional groups. The relative contribution of these mechanisms depends on the molecular size, hydrophobicity, ionization state, and aromaticity of the pollutant as well as the surface area, pore-size distribution, aromaticity, pH, and functional-group chemistry of the biochar [19].

In PAH-contaminated soil used for carrot cultivation, corn-straw biochar produced at 300 °C (CB300) and bamboo biochar produced at 700 °C (BB700) significantly reduced the accumulation of high-molecular-weight PAHs in carrot roots after 150 days, demonstrating that biochar can interrupt soil-to-plant transfer [16]. In vegetated PAH-contaminated soil, straw biochar reduced total PAH bioavailability by 70.3%, whereas willow biochar produced a 29.3% reduction; activated carbon produced a 38% reduction under the conditions examined [15]. These differences emphasize that feedstock and production conditions strongly affect sorption performance and that biochars should not be treated as a single uniform material.

Biochar has also been evaluated for ionizable organic contaminants. In sulfamethazine-contaminated soil, burcucumber-derived biochar produced at 700 °C (BBC700) reduced sulfamethazine uptake by lettuce by up to 86% [14]. Such reductions in plant uptake and dissolved concentrations can lower immediate exposure and restrict transport toward groundwater. Nevertheless, sorption does not necessarily represent permanent removal: aging of biochar, competition with natural organic matter, changes in soil pH, and contaminant desorption may alter long-term retention. Therefore, remediation assessments should distinguish between short-term decreases in bioavailability and long-term contaminant fate and should include monitoring of desorption, transformation products, and potential ecological effects [19].

Overall, the remediation performance of biochar results from the interaction between contaminant chemistry and biochar physicochemical properties. For heavy metals, immobilization is dominated by sorption, complexation, ion exchange, precipitation, and related surface interactions; for organic contaminants, pore filling, partitioning, hydrophobic and π-based interactions, hydrogen bonding, and electrostatic forces are particularly important. Modification strategies can enhance selected mechanisms, but their effectiveness should be assessed under realistic soil conditions and over sufficiently long time scales to confirm durable risk reduction.

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