

## Review

# A review and bibliometric analysis on recent modification of biochar for effective and sustainable remediation of heavy metals in aqueous medium

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## Abstract

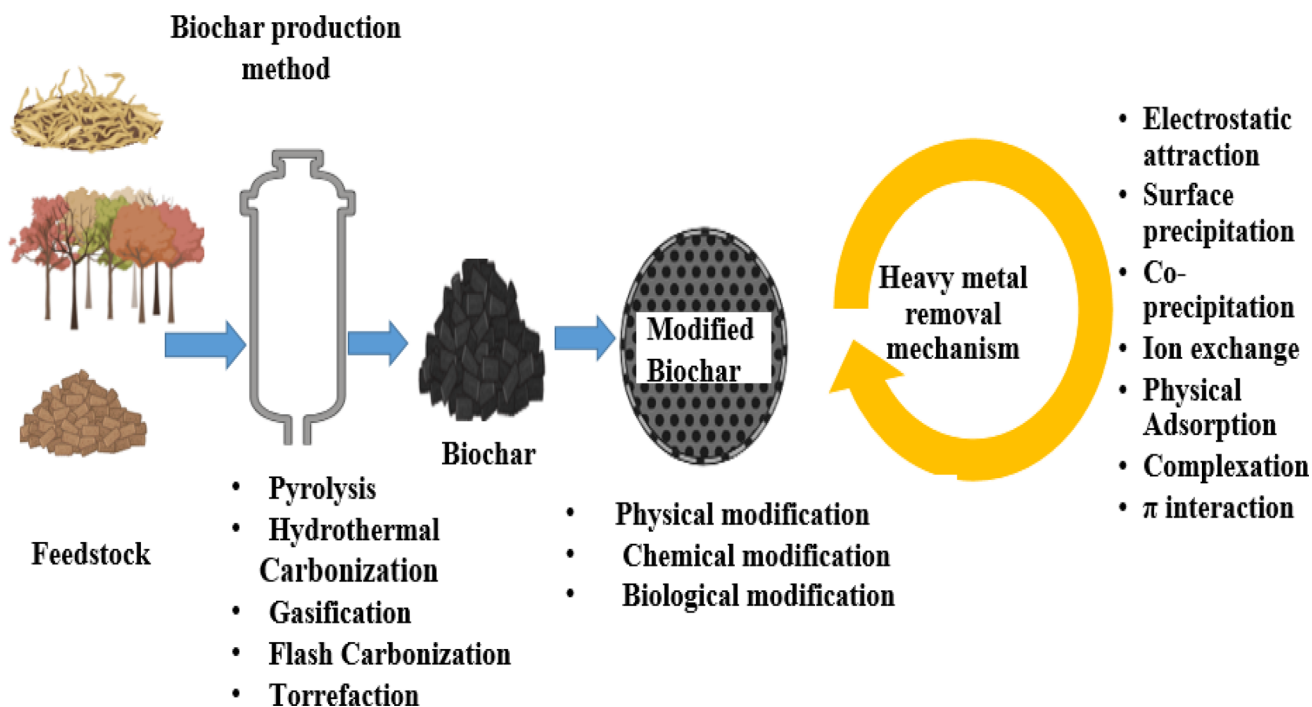
Worldwide, one of the leading environmental concerns is heavy metal contamination in water, which endangers both the ecosystem and human health. The techniques for the remediation of heavy metal contamination are ion exchange, solidification, precipitation, adsorption, and electrochemical reduction. Biochar is an environmentally friendly and cost-effective sorbent that effectively adsorbs heavy metals from water. It is derived from various biomass sources, including sewage sludge, agricultural residues, industrial waste, forest products, and aquatic waste. Despite having properties like functional groups, and potential for heavy metal removal, biochar has limited specific surface area, functional groups, and porosity. Modifying the biochar surface can improve its physicochemical qualities by altering its functional groups, active sites, porosity and enhancing heavy metal adsorption ability. The average removal efficiency of modified biochar ranging from 75 to 95%, depending on modification type, biochar feedstock and experimental conditions. With these qualities, modified biochar can effectively remediate heavy metals via ion exchange, surface precipitation, electrostatic attraction, co-precipitation, complexation, physical adsorption, and  $\pi$  interaction. The review paper presents a comprehensive overview of the diverse feedstocks utilized for biochar synthesis, various methods of biochar production, and the recent physical, chemical, and biological activation techniques. A bibliometric analysis is provided to understand recent trends in using biochar for the remediation of heavy metals at the global level. This article briefly discusses the sorption mechanism involved in heavy metal contaminant removal. Furthermore, regeneration strategies and the reusability of modified biochar are summarized to promote sustainable development. Future research directions are proposed for more efficient use of biochar in practical wastewater treatment.

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## Graphical Abstract



## Highlights

- Agro-waste based biochar promotes eco-friendly removal of heavy metals from wastewater and help to achieve SDG-6.
- The chemical modification of biochar shows better enhancement of surface area, pore size, and functional groups.
- SEM, XRD, FTIR, BET and XPS studies confirmed the enhanced heavy metals adsorption efficiency of modified biochar.
- Biochar's regeneration and reuse, aid environmental sustainability.
- Bibliometric analysis evaluated the trends in research for biochar activation for heavy metals remediation.

**Keywords** Modified biochar · Scientometric analysis · Heavy metal adsorption · Water purification · Green adsorbent · Sustainability

## 1 Introduction

Water is a crucial component for the survival of life on Earth. Rapid urbanization, industrialization, and an exponential expansion in the human population cause many environmental challenges, including water contamination and scarcity. In a recent report released jointly by the United Nations Children's Fund (UNICEF) and the World Health Organization (WHO), it was revealed that 2.1 billion people globally, that is, 25% of the global population, have not access to readily available, safe drinking water at home [1]. Heavy metal contamination in water is becoming a significant ecological and public health concern due to its non-biodegradable and toxic nature, even in trace amounts. Exposure to heavy metals in the living system has increased dramatically in recent decades due to the rapidly growing use of heavy metals in various sectors like industries, agriculture, household, and technical sectors. The different sources of heavy metals are industrial wastewater released by paper mills, metal processing, tanneries, fertilizers, textile mills, mining, and pharmaceutical sectors [2]. Inhalation, ingestion, nutrition, or carelessness are critical routes by which heavy metals can the organisms [3].

Heavy metals concentration, physical and chemical characteristics in water, and their different oxidation state determine their toxicity. Furthermore, heavy metals in an aqueous medium may form heavy metals-antibiotic resistant bacteria. These bacteria are microorganisms that grow in heavy metal-contaminated sites and enhance the level of antibiotic resistance, causing concern to the environment and public health [4].

The primary toxic heavy metal contaminants in water include arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn). These metals are responsible for ecological and carcinogenic health risk, as shown in Fig. 1. The health impacts of heavy metal exposure on human health include neurotoxicity, which affects the neurological system, and genotoxicity, which can harm genetic material like DNA. Other effects include hepatotoxicity (liver damage), nephrotoxicity (kidney damage), carcinogenicity (cancer risk), pulmonary toxicity (lung damage), preterm birth risks, and cardiovascular toxicity (affecting the heart and blood vessels) [5].

Ion exchange, chemical or physical precipitation, electrochemical reduction, and adsorption are conventional methods for the remediation of heavy metals [4]. Among these techniques, adsorption is considered one of the most widely used methods due to its ease of use with high pollutant removal efficiency [6]. To support sustainable treatment approaches, there is a need for the development and use of accessible, low-cost, and renewable adsorbents. Using agricultural waste and residues in adsorbents aligns with green chemistry principles and circular economy, offering a renewable and eco-friendly solution [7].

Biochar is a green adsorbent rich in carbon and produced in low oxygen condition such as plant waste, animal waste, agricultural residues, and forest waste [8]. It is an effective and eco-friendly adsorbent for removing many contaminants, including heavy metals [9]. Adsorption using biochar is a feasible and long-term replacement for conventional heavy metal removal techniques. Over the past ten years, there has been a substantial advancement in the research on using biochar for water remediation. When compared to traditional approaches, this indicates a practical green solution with greater removal efficiency and sustainability [10]. However, research has shown that pristine biochar has a limited adsorption capacity, and modification is required to increase the adsorption effectiveness. The physical, chemical, and biological activation methods modify pristine biochar. The alteration increases the porous volume, specific surface area, functional group diversity, surface reactivity, and heavy metal removal capacity of the biochar [11].

Biochar's application focuses on four Sustainable Development Goals (SDGs) out of 17: SDG-6 (clean water and sanitation), SDG-7 (affordable and clean energy), (SDG-12) responsible consumption and production, and SDG-13 (climate action). The rapid rise of industries has released massive volumes of effluent that degrade water quality into the

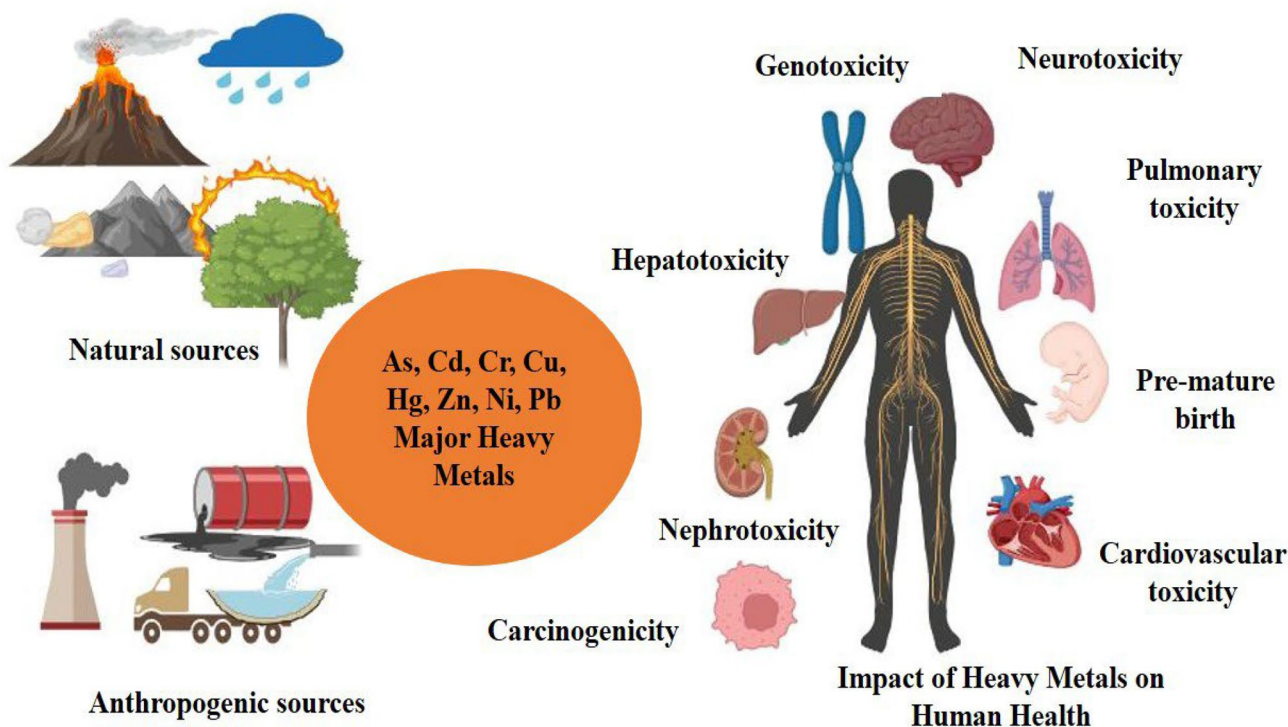


Fig. 1 Major sources of heavy metals with their potential effects on human health

environment matrix. As a result, wastewater treatment is essential to achieve the SDG-6 goal [12]. Biochar is a green adsorbent that reduces greenhouse emissions as it is prepared from waste material. Biochar and its modification-based remediation of heavy metals in water help to achieve the SDG-6 goal [13]. The primary goal of this review study is to examine recent modification in biochar to eliminate heavy metals from aqueous system. Numerous biochar feedstocks and manufacturing processes have been thoroughly researched. Various biochar activation methods have been summarised, including physical, chemical, and biological alterations that boost remediation efficiency. The study discusses the mechanism of heavy metal adsorption using modified biochar and regeneration options for adsorbent recycling. Furthermore, this article examines the reusable nature of modified biochar as an economic factor for large-scale manufacturing for environmental sustainability. Finally, research gaps and potential future directions are thoroughly explored.

## 2 Bibliometric analysis

A bibliometric analysis is done to study literature gaps and research trends in applying modified biochar as a sorbent to mitigate heavy metal ions in wastewater. The different parameters of bibliometric analysis, such as annual scientific production, the most frequent words (word cloud), the country's collaboration map, and trend topics in the biochar field, were studied using Biblioshiny, a web-based interface for Bibliometrics (R-software-based tool). A keyword co-occurrence network is created using VOSview to study the most highlighted area in the biochar field [14].

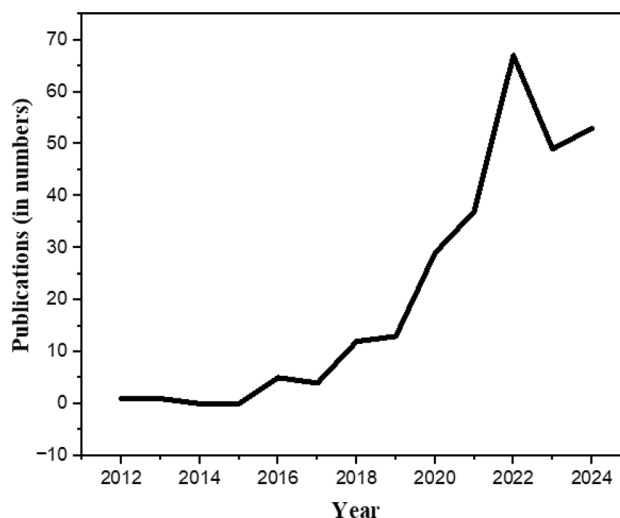
### 2.1 Annual scientific production

The keywords “modified biochar for heavy metal removal in aqueous medium” were used on the Scopus database for a literature review and depict the annual scientific production report from 2012 to 2024. Two hundred seventy-one research papers were published before September 2024 in this field, as shown in Fig. 2.



Fig. 2 An overview of primary information collected through data analysis in biblioshiny

**Fig. 3** The number of publications published on “modified biochar for heavy metal removal” from 2012 to 2024.  
Source: Science Direct



The scientific production during the initial years was minimal. From 2017 onwards, there has been a sharp and continuous increase in research publications, reflecting growing interest and advancement in this field as shown in Fig. 3.

## 2.2 Keyword co-occurrence network

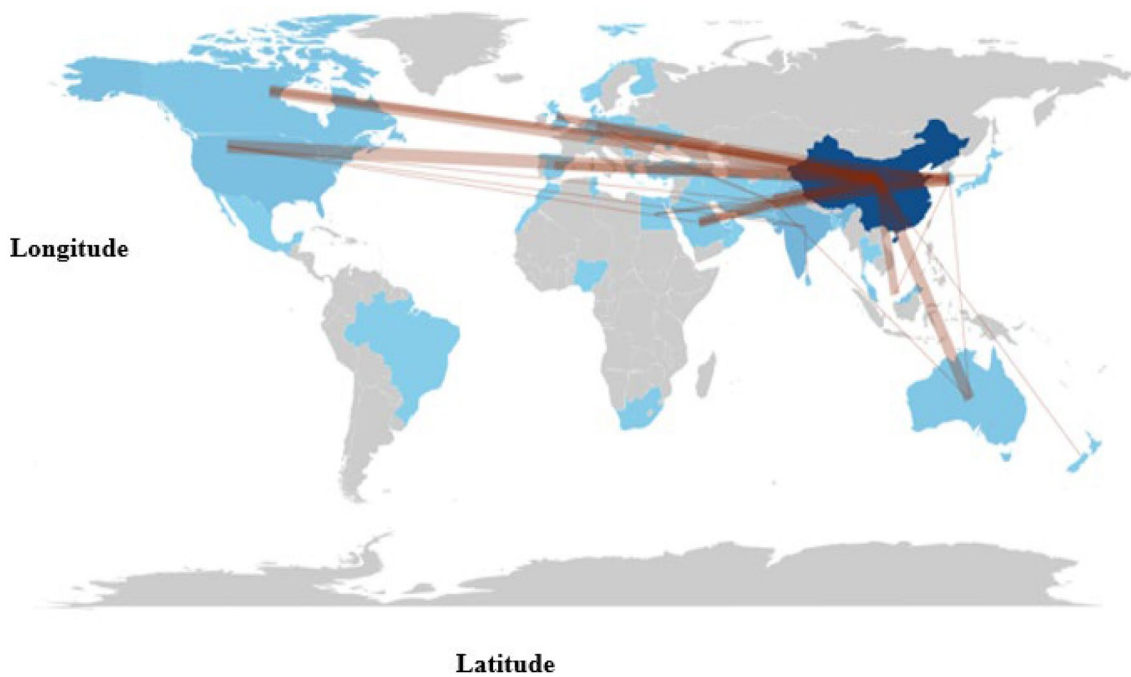
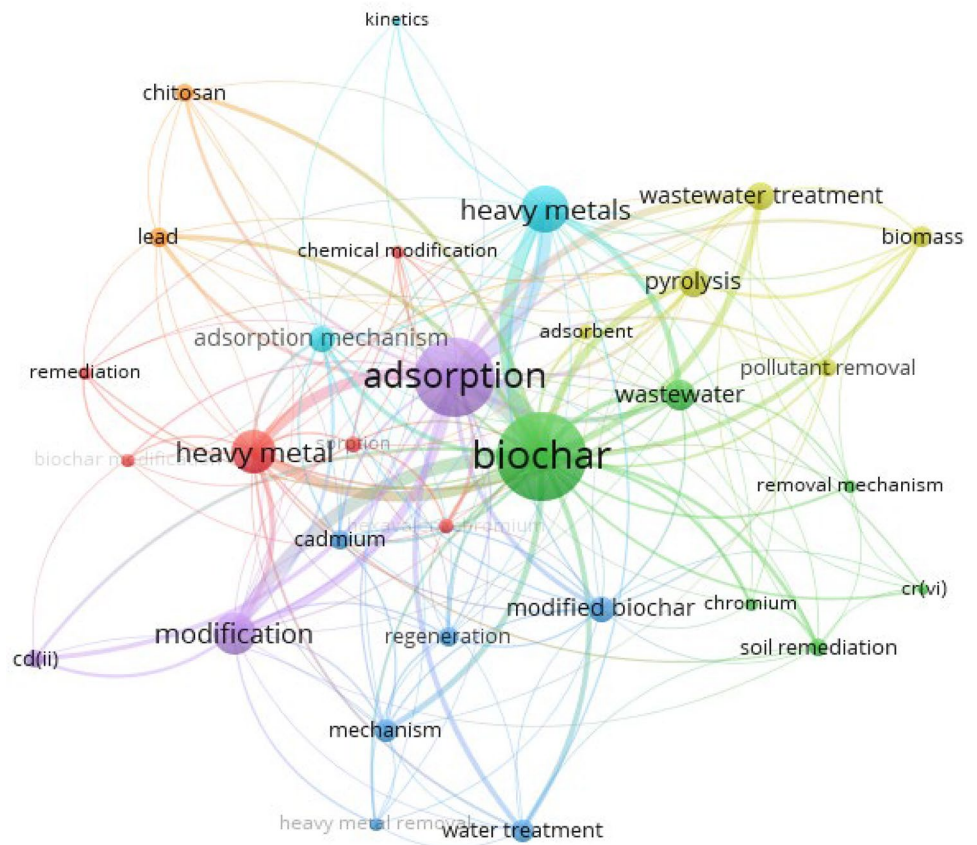
The co-occurrence approaches in this review article investigate the emerging research trends in the biochar field using keywords provided by the authors. A minimum threshold of 5 was set for the number of occurrences per keyword to collect meaningful results. The size of the node indicates how frequently the keywords are used in the research articles, and the linkage between nodes represents the association between keywords. The emerging research trends in an area using keyword co-occurrence analysis can be predicted. This is accomplished by incorporating important keywords from future research directions specified in publications. The study performed with VOSview 1.6.20. Software [15] reveals that adsorption is the commonly used process used for heavy metals remediation in the aqueous system by biochar, as shown in Fig. 4. This extensive study uses keyword co-occurrence approaches to highlight major themes and provide a road map for future research goals.

## 2.3 Country's collaboration world map and trend topics

The collaboration map demonstrated that biochar and its modification-based heavy metal ions adsorption is a worldwide recognized research field. The maximum research collaborations are seen between China-Pakistan, China-Australia, China-Korea, China-USA, China-Canada, Pakistan-Malaysia, Pakistan-Saudi Arabia, China-Germany, China-Hong Kong, USA-Pakistan, India-Sri Lanka, India-USA, USA-Saudi Arabia, Australia-Egypt, Korea-Egypt, Australia-Germany, and Australia-Spain as shown in Fig. 5. The research collaboration map shows that the most significant contributor country in the field of biochar is China, ahead of the United States, Australia, Pakistan, India, and South Korea. The analysis also emphasizes the relevance of international research collaboration and helps researchers to build new partnerships.

Trend topics provide insightful information about where the focus of academics is moving around and help researchers in pivoting their efforts towards high impact areas. The growth of hot subjects in the field of biochar from year 2016 to 2024 is shown in Fig. 6, created using Biblioshiny. Trending topics discovered from the collected literature were “adsorption,” “biochar,” “modification,” “aqueous solution,” “charcoal,” “biomass,” and “heavy metal removal”. The term frequency denote the most repeated word in the literature. According to the data, a significant portion of academic researchers focus on studying wastewater treatment through biochar modification for heavy metals elimination.

**Fig. 4** A bibliometric co-occurrence network was created using VOSview, and 271 results were collected from the Scopus database (from 2012 to 2024) using terms like biochar, modification, aqueous medium, and heavy metals as keywords



**Fig. 5** The world map shows countries' collaboration in biochar and its modification for mitigating heavy metals in water



## 2.4 Word cloud

Word clouds are frequently used by researcher to find out key themes and trend topics in the published literature. It represent the frequency of keywords and these keywords highlights the most prominent area in the field [16]. The larger and most central words in the word cloud represent the maximum appearance of the term in different research articles. This bibliometric analysis help in identifying emerging research areas, dominant keywords which are necessary to understand the recent trend of research. A minimum of five occurrences was set for each keyword to appear in the word cloud visualization using biblioshiny software. This strategy is shown in Fig. 7, uses the square root of each keyword's frequency to produce a more balanced and understandable representation of the most essential phrases. The resulting keywords focus on the current research area, specifically novel water treatment techniques. Biochar and its modification are highlighted for their ability to absorb heavy metals. The use of essential terminology like "water treatment" and "biochar modification" emphasizes the importance of these procedures and the researchers' focus on increasing biochar efficacy through numerous modifications. The diversity of keywords indicates increasing research on using modified biochar for removal of heavy metals in aqueous system.

## 3 Biochar synthesis methods

The synthesis of biochar includes the thermochemical breakdown of biomass. The biomass is firstly heated in oxygen-limited conditions to produce biochar, bio-oil, and syngas. The required properties of the biochar and the equipment's accessibility determine the precise technique of biochar production [3]. Different types of feedstocks are used to produce biochar. The most commonly used feedstocks for biochar are sewage sludge, animal wastes, forestry residues, and agricultural residues. The feedstock selection is influenced by several factors, such as cost, availability, and desired biochar quality [17]. The feasibility of modification techniques is impacted by the kind of feedstock (wet or dry), so it is crucial to classify biomass feedstock to manufacture biochar. Agricultural leftovers and some wood species (low moisture content, less than 30%) are widely used dry feedstocks; in contrast, wet biomass, like vegetable wastes, animal wastes, algae, and sewage sludge having high moisture content, more than 30% [18].

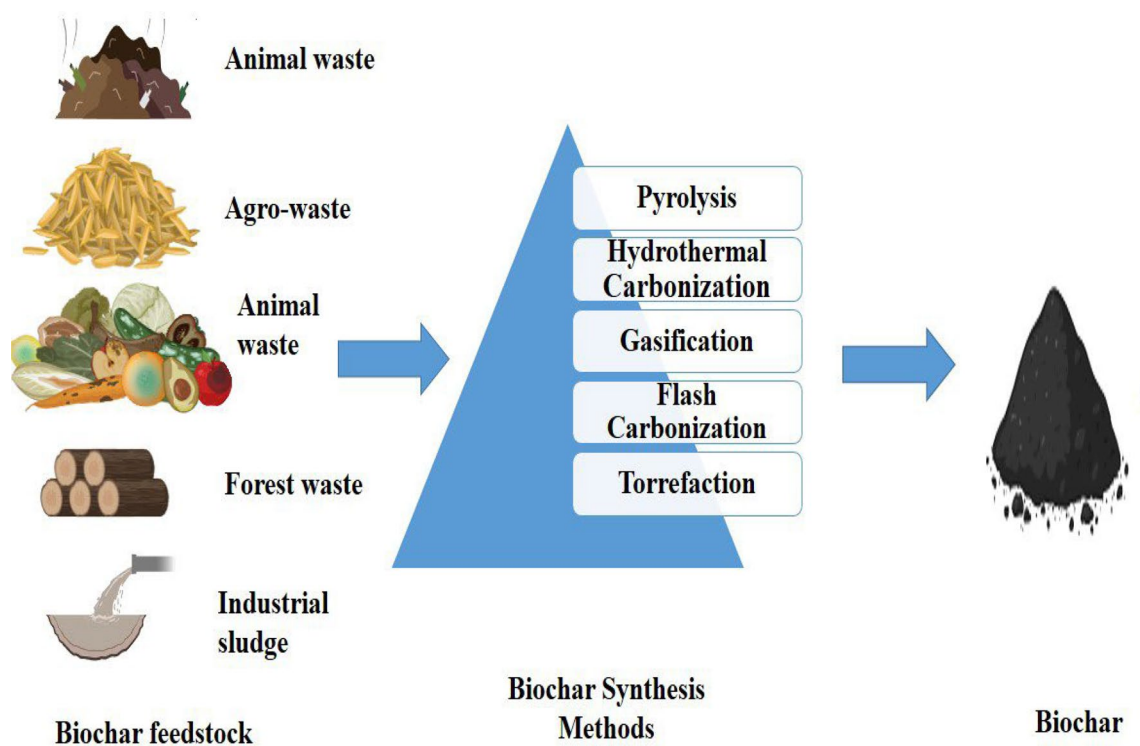


Fig. 8 Feedstock of biochar with different biochar generation methods

**Table 1** Different methods are used for the synthesis of biochar

Methods	Time	Temperature (°C)	Biochar yield %	Advantages	Disadvantages	References
Pyrolysis	1–24 h	300–900	12–35	Simple, easy to operate, good biochar yield	High-temperature pyrolysis causes deactivation of functional groups	[23, 24]
Hydrothermal carbonization	1–16 h	180–300	80	High-yield biochar with a large number of oxygen functional groups	Required to optimize heat and pressure	[25]
Gasification	10–20 s	700–900	10	Inexpensive, low residence time	Low yield of biochar	[26]
Torrefaction	10–60 min	200–300	80	decrease the volatile contents from the biomass, high biochar yield	Hygroscopicity, and limited processability	[27]
Flash carbonization	30 min	300–600	28–32	Short residence time, low temperature maintain	High pressure required	[22]

The most frequently used methods for biochar synthesis are pyrolysis, gasification, hydrothermal carbonization, flash carbonization, and torrefaction, as shown in Fig. 8 and Table 1. The most popular pyrolysis technique entails heating biomass in an oxygen-limited environment. Hydrothermal carbonization is a technique that uses hot and pressurized water to convert biomass into hydrochar products [19]. The reaction occurs at temperatures ranging from 180 to 300 °C and 10 to 25 MPa pressures. Gasification uses moderate oxidizing agents, like oxygen, and heats the material to temperatures between 700 and 900 °C [20]. Torrefaction is similar to pyrolysis as it occurs without oxygen but requires low temperature and standard atmospheric pressure and is commonly referred to as mild pyrolysis [21]. Flash carbonization involves heating biomass at 300–600 °C temperature for 30 min [22].

### 3.1 Pyrolysis

The thermal decomposition of biochar at high temperature (300–900 °C) in absence of oxygen known as pyrolysis. The biomass used for biochar production mainly contains lignin, cellulose, and hemicellulose, which undergo cross-linkage, polymerization, and fragmentation during pyrolysis. The main products of this method are biochar, bio-oil, and syngas [23]. Pyrolysis is classified into three categories based on residence time and heating time: fast, intermediate, and slow. Figure 9, shows different product get formed from pyrolysis process.

#### 3.1.1 Fast pyrolysis

A fast thermochemical method liquefies carbon biomass to produce bio-oil as the main product [28]. The fast pyrolysis process is performed under the following conditions: quick heating of the biomass (>100 °C/min) [29], moderate temperature (400–600 °C) [30], and short residence time (0.5–2 s) [31]. The requirement to shorten the fume residence time in the hot zone in order to generate high-quality bio-oil is a crucial characteristic that sets fast pyrolysis apart [22].

#### 3.1.2 Intermediate pyrolysis

Intermediate pyrolysis produces more liquid fuel and less biochar than slow pyrolysis since it occurs at low temperatures (500–650 °C) and short residence period (10–20 s). A longer vapor residence time is necessary to reach the requisite temperature and finish the pyrolysis [18]. The quality of end products increased with intermediate pyrolysis because a chemical reaction occurs in controlled conditions and produces only 20% biochar, 30% biogas, and 50% bio-oil [32].

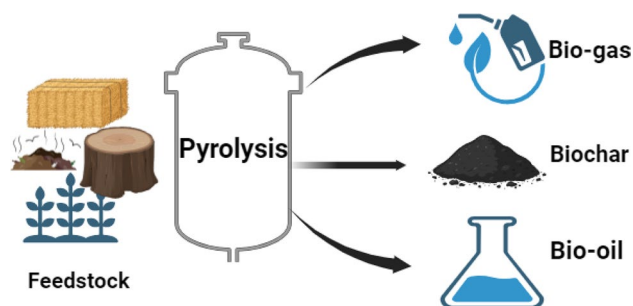
#### 3.1.3 Slow pyrolysis

Slow pyrolysis is an effective method to produce biochar. The process occurs at a slow heating rate (5–7 °C/min), with residence time (more than 1–24 h), and temperature (300–700 °C). Biochar's productivity in slow pyrolysis is higher than that of other pyrolysis techniques due to the decreased thermal cracking of feedstock and slower heating rate [33].

### 3.2 Hydrothermal carbonization

It is a thermochemical treatment that requires both pressure (2–10 MPa) and heat for the thermal breaking of biomass into biochar in the presence of water at 180–300 °C without pre-drying [25]. The hydrothermal carbonization method is spontaneous and exothermic, and the presence of water produces biochar with more chemical functional groups.

**Fig. 9** Overview of the pyrolysis process



The traditional slow-pyrolysis method of drying biomass residue and producing biochar can be substituted with this approach as it produces a stable byproduct that is rich in carbon. Here, water plays a critical role in the hydrolysis of the glycosidic group found in the cellulose and hemicellulose of the biochar feedstock [34]. The biochar which is synthesised by the hydrothermal process is known as hydrochar, which has low carbon with higher stability, high porosity, lower ash content, and low specific surface area [35, 36].

### 3.3 Gasification

It is a chemical process in which carbon-containing biomass gets converted into solid (biochar), liquid (bio-oil), and gaseous (syngas) products at high temperatures (700–900 °C). The gasification process includes four main stages: drying of biomass, pyrolysis, partial oxidation of biomass, and biomass reduction [37]. There are three main gas–solid contact modes in gasification reaction: fixed bed, inlet flow, and liquefied bed. The main product of this method is syngas, which is approximately 85% of the biomass. This method is less expensive and requires low residence time (10–20 s) [38]. The major limitation of this method is the low yield of biochar (5–10%), which requires optimization conditions, such as pressure, temperature, and composition of the reactive gases [39].

### 3.4 Torrefaction

Thermochemical torrefaction occurs at modest heating rates and temperatures between 200 and 300 °C in an inert atmosphere. It enhances biomass's hydrophobicity, milling qualities, and energy density [27]. The procedure eliminates moisture and partially decomposes the lignocellulosic components of biomass by releasing some volatiles, resulting in a final solid product known as 'torrefied biomass' or simply biochar [40].

### 3.5 Flash carbonization

This thermochemical method turns biomass into solid and gas phase products at 300–600 °C by maintaining a high pressure of 1–2 MPa. In the flash carbonization method, the combustion flame moves against the gas stream (upward movement of flame), quickly converting the feedstock materials into gas [41]. The biochar yield is about 28–32%, which is moderate compared to conventional carbonization methods. The primary benefits of this technology are that it requires short residence time (less than 30 min) and low temperature for heating biomass [42].

## 4 Recent biochar modification methods

There are a lot of scientific studies on the use of biochar; these current studies have mainly concentrated on the alteration of biochar to improve its specific surface area, functional groups, porosity, and heavy metal adsorption efficiency. There are numerous methods for modifying biochar, which can be classified into three categories: physical, chemical, and biological, as discussed in Fig. 10.

### 4.1 Physical treatment techniques

In physical treatment, biomass is dried, crushed, sieved, and washed to remove impurities [43]. This procedure is often simple and cost-effective, as it does not use costly chemicals throughout the alteration process, but their adsorption efficiency is lower than chemically modified biochar. Physical modification techniques frequently used are ball milling, gas filling, and steam activation [44].

#### 4.1.1 Ball milling

It is an effective method based on the kinetic energy of a moving ball to change particle shape, break chemical bonds, and synthesize nanosized biochar. It improves biochar's adsorption capacity by enhancing properties like specific

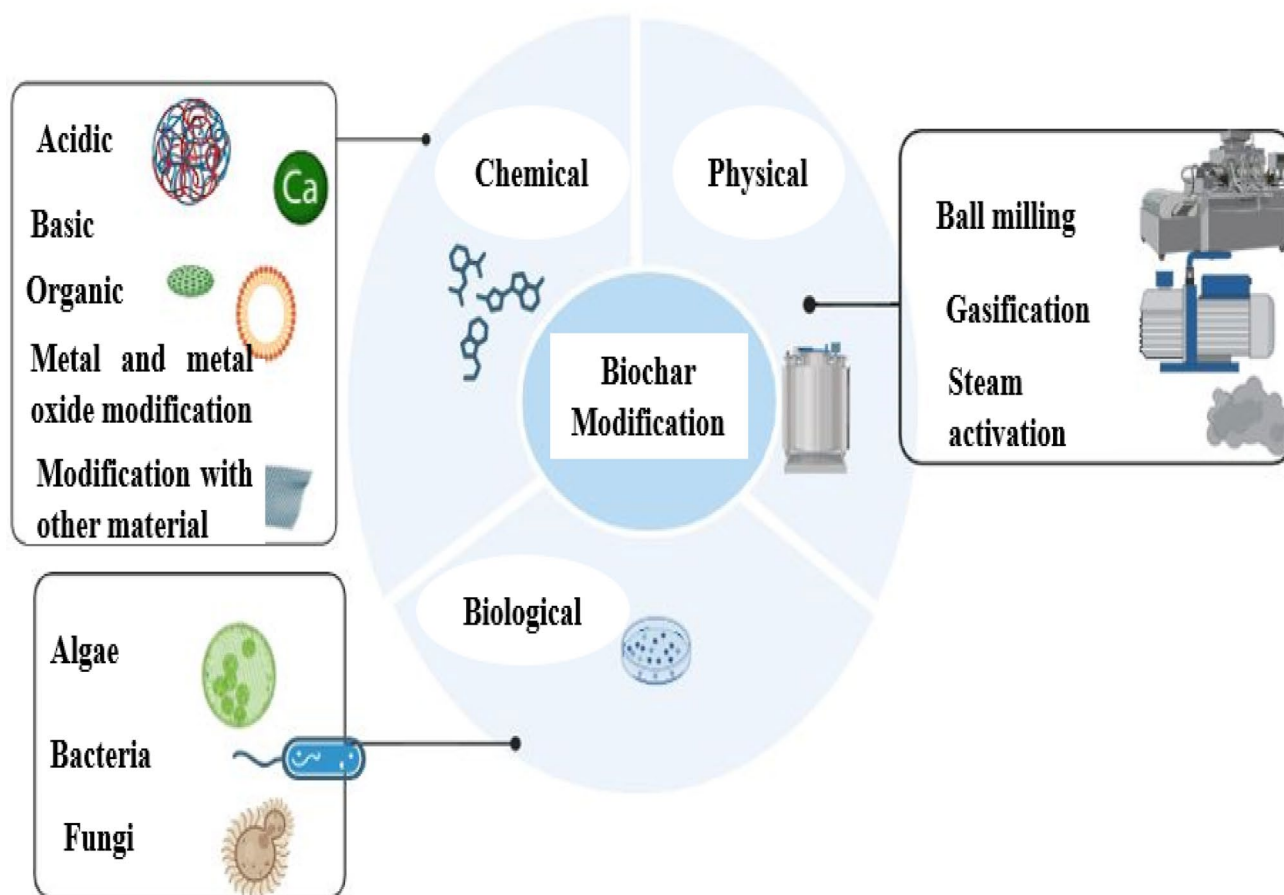


Fig. 10 Biochar modification methods

surface area, zeta potential, micropore surface, volume of pore, and functional groups [45]. Li et al. used ball-milled magnetic nano biochars to study the adsorption of Hg(II) from an aqueous solution. The adsorption capacity for Hg(II) was 127.4 mg/g. Electrostatic attractions, surface complexation, and Hg–C $\pi$  bond formation were the primary mechanisms for sorption [46]. Cui et al. studied the effect of ball milling on Cd(II) ions' sorption from aqueous solution using layered double hydroxides' biochar composites. They found increased specific surface area and adsorption capacity (119 mg/g). The kinetic experiments demonstrated that the Cd(II) elimination by modified biochar occurred through both physical and chemical sorption mechanisms [47].

#### 4.1.2 Gas filling

The gas-filling process introduces CO<sub>2</sub>, N<sub>2</sub>, and other gases into the biochar to improve its microporous structure, specific surface area, pore size, and pore volume [44]. Islam et al. studied the effect of biochar modification with CO<sub>2</sub> and N<sub>2</sub> gas. The biochar was prepared using rice straw and pulp mill sludge. The adsorption capacities of N<sub>2</sub> gas-modified rice straw and pulp mill sludge for Pb(II) were 133.3 mg/g and 256.4 mg/g, respectively, which were slightly higher in comparison to the adsorption capacities of modified CO<sub>2</sub> gas rice straw and pulp mill sludge (109.9 mg/g and 250.0 mg/g respectively) [48].

#### 4.1.3 Steam activation

The process is performed without oxygen with temperatures ranging from 400 to 800 °C to increase biochar's specific surface area, porosity, and surface morphology. This modification method improves biochar's adsorption capacity by

forming mesopores and macropores on the biochar's surface, increasing biochar's cation exchange capacity [49]. The basic mechanism of steam activation is described in Eqs. (1) and (2) [50, 51].



The opening of the pores in the carbon structure increases the biochar's specific surface area when this procedure is repeated several times. Steam modification removes volatile gases or particles trapped on the biochar surface to increase pore volume. However, its poor carbon yield, high temperature, and energy requirements limit its widespread implementation [52]. Wang et al. modified the biochar with steam activation at 500 °C for 45 min, and this modified biochar effectively adsorbs Cu(II) ions from wastewater with an adsorption capacity of 94.66 mg/g [53]. Kwak et al. compared non-activated biochar and steam-activated biochar for the adsorption of Pb(II). The adsorption efficiency of steam-activated biochar is nearly two times more than non-steamed biochar's [54].

## 4.2 Chemical treatment techniques

Chemical modification includes the treatment of biochar with acid, base, metal oxides, and organic compounds to change its pore volume, specific surface area, functional groups, and binding sites for better remediation of heavy metals [55]. This method is frequently used for biochar modification but is a complex, expensive procedure involving toxic reagents.

### 4.2.1 Acidic modification

Acidic modification is commonly used to modify the biochar by immersing it in a strong acid like hydrochloric acid (HCl), phosphoric acid ( $\text{H}_2\text{PO}_4$ ), nitric acid ( $\text{HNO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), citric acid, oxalic acid, etc. [56]. The acid treatment method adds different functional groups on the surface of biochar, increasing its acidity, altering its porous structure, and enhances the heavy metal ions sorption capacity by complexation and ion exchange mechanism [57]. It has been observed that the modification of biochar with  $\text{H}_3\text{PO}_4$  acid changes the functional groups, pore size, and elemental composition of biochar, which enhances the adsorption of Pb(II) and Cd(II) [58]. The adsorption of Cd(II) on the surface of biochar was efficiently enhanced by the alteration of the  $\text{HNO}_3/\text{H}_2\text{SO}_4$  solution (1:1), which increased carboxyl functional groups [59].

### 4.2.2 Basic modification

Basic modification involves immersing biochar in a stronger base like NaOH, KOH, and  $\text{Ca}(\text{OH})_2$  [60]. The base alteration increases surface oxygen content, pore volume, specific surface area, pH, dissolved ash content, and organic groups [61]. Compared to acidic modified biochar, the base treatment creates biochar with a larger specific surface area, greater surface aromaticity (H/C) ratio, higher N/C ratio, and lower O/C ratio [62]. The commonly used base for the modification of biochar is potassium hydroxide (KOH) and sodium hydroxide (NaOH) [57]. The modified N-enriched biochar made from leftover chicken feathers using KOH that boost the adsorption capacities of Cd(II) and Pb(II) by 7.07 and 26.52 times, respectively, than to the original biochar, 22.32 mg/g for Cd(II) and 119.65 mg/g for Pb(II) [63]. The KOH—activated modified biochar increased the sorption of Pb(II), Cd(II), and Cr(VI) up to 140.0, 127.2, and 29.0 mg/g, respectively, at the optimum pH values for each heavy metal [64]. The addition of  $\text{KMnO}_4$  and KOH to biochar increased the carboxylic group on the surface, resulting in higher adsorption efficiency of As(V) (91.26%) and As(III) (86%) [65].

### 4.2.3 Metal and metal oxide modification

Biochar adsorption, and magnetic properties can be modified with metals and metal oxides. The activation enhances the biochar properties like nitrogen-containing functional groups and ion exchange capacity for better remediation of heavy metals [66]. The two main methods of modifying materials with metals and metal oxides are as follows: (1) combining the metals or metal oxides with raw materials and pyrolyzing the mixture to create biochar, or (2) biochar immersed with metal ions or metal oxides under specific conditions [67]. The use of metal and metal-modified biochar to remove heavy metals from an aqueous medium has been reported in earlier literature, as shown in Table 2.

**Table 2** A summary of recent articles on biochar metal and metal oxide modification for heavy metal removal

Biochar feedstock	Modifying agent	Temperature (°C)	Contact time (min)	Heavy metals	Adsorption capacity (mg/g)	References
Corn cob	MgCl <sub>2</sub> ·6H <sub>2</sub> O	450	1	Cu(II), Cd(II), Pb(II)	300.20, 178.97, 526.20 respectively	[68]
Oiltea camellia shell	Si	450	2	Cd(II)	211	[69]
Corn strover	Nano ZnO/ZnS	600	1	Pb(II), Cu(II), Cr(VI)	135.8, 91.2, 24.5 respectively	[70]
Rice husk	MgO	600	2	Cd(II), Zn(II), Cu(II), Cr(VI)	104.68, 104.38, 173.22, 47.02 respectively	[71]
<i>Eupatorium adenophorum</i>	Mg(NO <sub>3</sub> ) <sub>2</sub> and FeCl <sub>2</sub>	500	1	Cd(II), Pb(II)	156.60, 252.70	[72]
Straw	Mg	400	2	Cd(II)	223.7	[73]
Cotton stem	MgCl <sub>2</sub>	700	1	Cd(II)	178	[74]
Corn stalk	Mn	600	2	Cd(II)	192	[75]
Corn straw	Fe	500	2	Cr(VI)	23.1	[76]
Residue of white tea	Fe <sub>3</sub> O <sub>4</sub>	500	1	Pb(II), Cd(II)	81.6, 38.6	[77]
Tree leaves of phoenix	Fe <sub>3</sub> O <sub>4</sub>	200	8	Cr(VI)	55	[78]
Sawdust	Mo	600	2	Pb(II)	189	[79]
Sugarcane bagasse and corncob husk	Fe	600	3	As(II)	50	[80]

#### 4.2.4 Organic modification

Organic-modified biochar adsorbents are treated with organic chemicals such as lignin, thiol, pyromellitic dianhydride polyethyleneimine, cyclodextrin, and thiourea. Adding organic compounds with higher functional groups to biochar boosted the sorption sites and the adsorption capacity of biochar [81]. Direct and indirect surface modification are two easy-to-implement techniques that have been used to enhance heavy metals adsorption efficiency [66, 82]. Various functional groups are directly grafted on the biochar surface in direct organic biochar modification. Indirect surface modification of biochar is another more accessible way to introduce adsorption active sites and functional groups directly on the biochar surface. Chitosan is a popular organic modifier used in the production of modified biochar. It has  $-NH_2$  and  $-OH$  groups, which benefit heavy metal adsorption. The biochar modified with  $\beta$ -cyclodextrin–chitosan was observed to have good adsorption capacity (206 mg/g) for Cr(VI) removal due to the addition of carbonyl and amino functional group on the biochar prepared from walnut shell [83]. The 3-mercaptopropyltrimethoxysilane-modified biochar has a higher removal capacity for inorganic  $Hg^{2+}$  ions (175.6 mg/g) than pristine biochar (105.7 mg/g) [84]. The thiourea-modified biochar, produced by pyrolysis from swine sewage, enhanced Pb(II) adsorption efficiency by 32%. The findings demonstrated that the introduction of S-containing functional groups (C=S and  $-SH$  groups) was the primary cause of high Pb(II) removal [85]. Rice straw-based biochar adsorbents containing amino groups were created through a macromolecular reaction of pendant groups that enhanced the removal capacity of biochar for Cr(VI) ions from 34.90 to 140.39 mg/g [86]. Amino-modified biochar was synthesized by adding nitrogen functional groups onto the biochar surface, resulting in a five-fold improvement in the biochar's adsorption efficiency for Cu(II) ions [87].

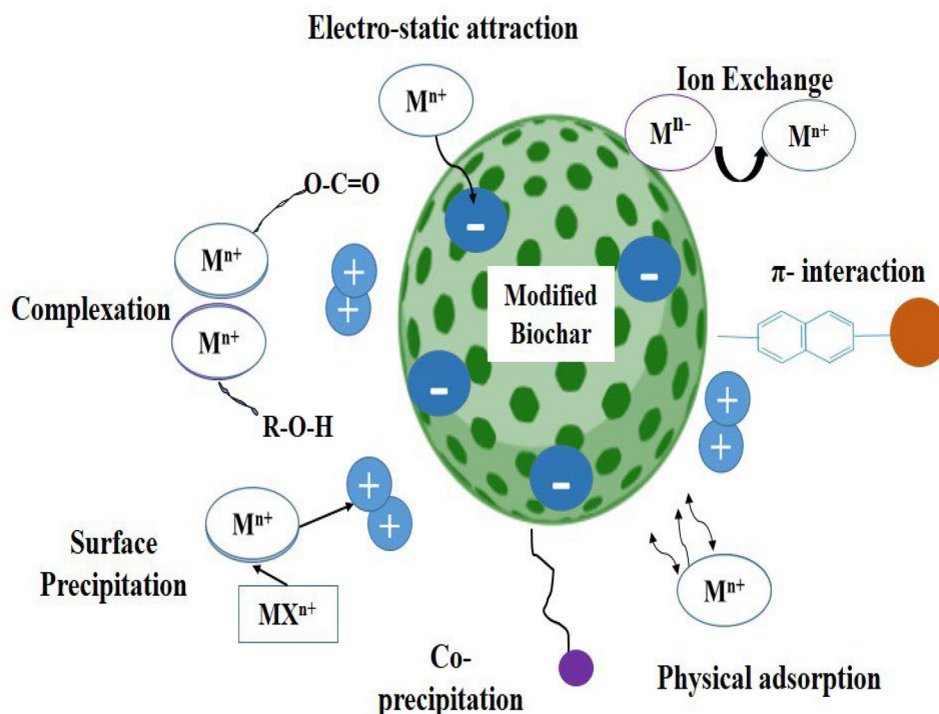
#### 4.2.5 Modification with other material

Materials such as carbonaceous material (graphene oxides), salts, and oxidants (hydrogen peroxide) are commonly used for biochar modification. Graphene oxide is produced during the production of graphene, Graphene oxide-based biochar composites have better sorption capacity for heavy metals (such as Cd(II), Co(II), Cu(II), Cr(VI), Pb(II), Zn(II), etc.) due to presence of oxygen-containing functional groups on its surface [88]. The modification of Water Hyacinth biochar with graphene oxide found better Cr(VI) sorption with an adsorption capacity of 150.02 mg/g [89]. The electrostatic attraction between the heavy metal ion and oxygen-containing functional group of graphene oxide is responsible for this enhanced sorption. The biochar modification with salts of chlorides, phosphates, etc., can also improve the surface chemistry and textual parameters of pristine biochar. Zhang et al. altered the biochar with inorganic potassium salt ( $K_3PO_4$ ) and performed pyrolysis at 550 °C for one hour in a nitrogen atmosphere. The  $HPO_4^{2-}$  breakdown resulted in the  $P_2O_7^{4-}$  enriched biochar that favors the better adsorption of heavy metals [90].

### 4.3 Biological modification

Using microorganisms to eliminate heavy metals from water systems has proven highly practical, cost-effective, straightforward, and promising. This approach is particularly effective for treating lower concentrations of heavy metals in water. The microorganisms such as yeast, algae, bacteria, and fungi are highly efficient at adsorbing heavy metals through their residual biomass. The biological sorption processes involve ion exchange, precipitation, physical adsorption, complexation, and cross-cell membrane transport. Several functional group sites exist on the microbial surface, including hydroxyl, carboxyl, amino, and carbonyl groups. This could potentially enhance the sorption effect of biochar by functional group exchange and surface grafting [91]. The biofilms of microorganisms (extracted from oil sand processed water), when colonized on biochar, increased arsenic adsorption up 6–7 times more than pristine biochar [92]. The effect of phosphate solubilizing bacteria (PSB) on the sorption of Pb(II) was studied by preparing an alkaline biochar using rice husk as feedstock and acidic biochar from sewage sludge and then modifying this biochar with PSB. This biological modification promoted stable pyroxenite formation on the biochar surface, increased the adsorption capacity, and found that the removal rate for rice husk biochar was 24.1% and sewage sludge was 60.85%. Thus, biochar modification with biological microorganisms is an effective way to remediate heavy metals [93].

**Fig. 11** Heavy metal ions adsorption mechanism of modified biochar



## 5 Adsorption mechanism for removal of heavy metals by modified biochar

According to studies, heavy metal ion adsorption by biochar can occur via electrostatic attraction, physical adsorption, surface precipitation, ion exchange,  $\pi$ -interaction, complexation, and co-precipitation, as shown in Fig. 11. It is greatly influenced by the type of heavy metal ions, the pore structure, and the different types of functional groups which are present on the surface of modified biochar.

The process of physical sorption involves the entrapment of heavy metals in the pores on the adsorbent surface through diffusional movement. The ion exchange is pivotal in removing heavy metals using modified biochar [94]. The presence of functional groups on the modified biochar surface, like hydroxyl, carboxyl, and phenolic groups, can undergo ion exchange reactions with heavy metal cations [10]. Surface precipitation is a crucial mechanism in removing heavy metals using modified biochar, and critical principles and various influencing factors govern its efficacy. The principle involves the interaction between heavy metal ions and the active sites present on the biochar surface [95]. Co-precipitation is a fundamental mechanism for removing heavy metals by modified biochar. The principle involves the formation of insoluble metal complexes through chemical reactions, leading to the precipitation of heavy metal ions [96]. The electrostatic adsorption mechanism is critical in removing heavy metals by modified biochar. The principle revolves around the attractive forces between charged metal ions and oppositely charged functional groups on the surface of the biochar, such as carboxyl, hydroxyl, and amine groups [10]. The complexation mechanism entails the complex formation of ligands on the surface of the modified biochar and heavy metal ions from wastewater [97]. The  $\pi$  interaction mechanism is crucial in removing heavy metals by modified biochar, particularly when the biochar surface is functionalized with aromatic groups or other  $\pi$ -electron-rich structures. This mechanism involves the attraction between the delocalized  $\pi$ -electrons in aromatic rings on the surface of biochar and the heavy metal ions in aqueous solutions.

Hu et al. synthesized biochar using pyrolysis process from peanut shell, crayfish shell, cotton stalk and corn cob. Sodium sulfide ( $\text{Na}_2\text{S}$ ) was used for biochar modification and Ni(II) was effectively removed from wastewater with adsorption capacity 15.40 mg/g. Brunauer–Emmett–Teller (BET) theory were used in the experimental study to determine specific surface area of adsorbent that was increased from 11.81 to 195.64  $\text{m}^2/\text{g}$  after modification. Higher surface area promote better adsorption. The X-ray photoelectron (XPS) and Fourier Transform Infrared (FTIR) spectroscopy results suggested that sulfhydryl and carboxyl groups get attached in biochar after modification. These functional groups responsible for removal of Ni(II) by ion exchanges and physical adsorption adsorption mechanism [98]. Xiao et al. removed Cr(VI) and

Cu(II) from aqueous solution using magnetic Loofah biochar activated with chitosan. The adsorption capacity of modified biochar was Cr(VI) was 30.14 mg/g and 54.68 mg/g for Cu(II). The XPS study revealed that surface complexation and ion exchange were the main adsorption mechanism [99]. Zheng et al. used chitosan and ethylene diamine tetraacetic acid (EDTA) to modified magnetic biochar which was prepared using peanut shell and ferric chloride ( $\text{FeCl}_3$ ). Scanning electron microscopy (SEM) images showed EDTA activated biochar were rough and porous, favours better adsorption. The adsorption capacity of improved biochar was 156.68 mg/g for Pb(II) removal, which was approx. 15 times higher than unmodified biochar (10.90 mg/g). The FTIR and XRD study described that functional groups like amide and carbonyl of modified biochar responsible for forming strong complexation for adsorption of Pb(II) ions in the aqueous solution [100]. Zhu et al. [101] prepared biochar from wheat straw and activated with goethite ( $\alpha\text{-FeOOH}$ ). The adsorption capacity of modified biochar for As(III) and Cd(II) was 67.2 mg/g and 39.3 mg/g respectively. Ion exchange and co-precipitation were the main removal mechanism of As(III) and Cd(II) ions in the aqueous medium was precipitation, complexation, cation exchange, and  $\pi$  interactions, 3-mercaptopropyl trimethoxysilane for removal of Pb and Cd heavy metal. The oxidized and thiolated biochar had better porosity and functional groups. The main adsorption mechanism according to were precipitation, complexation, cation exchange, and  $\pi$  interactions [102]. A novel adsorbent prepared by Zhang et al. using chest nut shell biochar and activated with tri sodium phosphate salt ( $\text{Na}_3\text{PO}_4$ ) for Cd(II) removal with adsorption capacity 112.78 mg/g. The study showed that adsorption process was monolayer, endothermic and chemisorption. The aromatization enhancement after modification of biochar responsible for Cd(II) adsorption by interaction with  $\pi$  electrons and lone pair electrons [90]. Kang et al. synthesized  $\text{KMnO}_4$  and hematite modified corn stalk biochar for adsorption of Zn(II) and Cd(II). The adsorption efficiency of modified biochar was 1.88 and 1.79 times higher for Cd(II) and Zn(II) respectively, than pristine biochar. X-ray diffraction (XRD) study that electrostatic interaction, co-precipitation, ion exchange, complexation and  $\pi$  interaction were the main adsorption mechanism [103].

Tian et al. developed biochar from corn straw and supported with sulfide nanoscale zero-valent iron for effective removal of Cr(VI). The XRD spectra confirmed crystalline nature of modified biochar and suggest that co-precipitation was the main adsorption mechanism. XPS study revealed that the studied heavy metal formed co-precipitates for their removal in the aqueous solution [104].

Wang et al. used macadamia nut shell as raw material for biochar synthesis for removal of Zn(II) ion in the aqueous solution by modified the biochar with carboxymethyl chitosan (CMC) and potassium ferrate ( $\text{K}_2\text{FeO}_4$ ). The FTIR and XPS study described that complexation and electrostatic attraction were the main adsorption mechanism. Zn(II) was removed from aqueous solution by forming complex amino group of biochar and Zn(II) ions and electrostatic between hydroxyl group and Zn(II) ions [105].

Masuku et al. synthesized pine corn biochar activated with zinc doped nickel ferrite for adsorption of Cr(VI) from leather and textile industrial wastewater. The BET study result investigated that the synthesized adsorbent has high surface area ( $104 \text{ m}^2/\text{g}$ ). FTIR analysis found that electrostatic attraction was the main removal mechanism. The experimental study suggested that adsorption was monolayer, endothermic, and spontaneous [106]. Zhang et al. derived biochar from tea stem and modified with KOH, HCl and potassium ferrate ( $\text{K}_2\text{FeO}_4$ ) for removal of Cu(II) and Zn(II) from aqueous media. The FTIR study results showed that hydroxyl and carboxylic groups get vibrated which formed complex with heavy metals. The main mechanism according to the study was complexation [77]. The adsorption mechanism discussed in various literature for removing heavy metal ions is mentioned in Table 3.

## 6 Regeneration and reuse of modified biochar

An adsorbent's regeneration and reuse can significantly lower operating costs and environmental pollution. There are now a few efficient ways to recycle or regenerate modified biochar. These methods mainly comprise the following five categories: (1) acidic treatment ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$ , etc.), (2) base and alkaline treatment ( $\text{NaOH}$ , ammonia water), (3) Salt treatment (EDTA), (4) organic solvent treatment and (5) combined method [50]. The regeneration method mentioned above, used for modified biochar recycling purposes, is presented in Fig. 12. The summary of the related process is mentioned in Table 4.

**Table 3** The heavy metal adsorption mechanisms using modified biochar

Biochar feedstock	Modifying agent	Heavy metals ions	Adsorption mechanism	References
Dried loofah sponges	Chitosan	Cu(II), Cr(VI)	Ion exchange and complexation	[99]
Peanut shell, cotton stalks, crayfish shell, and corncob	Na <sub>2</sub> S	Ni(II)	Ion exchange and physical adsorption	[98]
Wheat straw	α-FeOOH	Cd(II), As(III)	Ion-exchange, co-precipitation	[101]
Peanut shell	Chitosan-EDTA, FeCl <sub>3</sub>	Pb(II)	Complexation	[100]
Pig manure	3-Mercaptopropyl trimethoxysilane	Pb(II), Cd(II)	Precipitation, complexation, cation exchange, and π interactions	[102]
Chest nut	Sodium salt (Na <sub>3</sub> PO <sub>4</sub> )	Cd(II)	π interaction	[90]
Corn stalk	KMnO <sub>4</sub> , hematite	Cd(II), Zn(II)	Electrostatic interaction, co-precipitation, ion exchange, complexation and π interaction	[103]
Corn straw	Sulfide nano-scale zerovalent iron	Cr(VI)	Co-precipitation	[104]
Macadamia nut shell	CMC, K <sub>2</sub> FeO <sub>4</sub>	Zn(II)	Electrostatic attraction, complexation	[105]
Pinecone biomass	Zn-Ni ferrite	Cr(VI)	Electrostatic attraction	[106]
Tieguanyin tea stem	KOH, HCl, K <sub>2</sub> FeO <sub>4</sub>	Cu(II), Zn(II)	Complexation	[77]

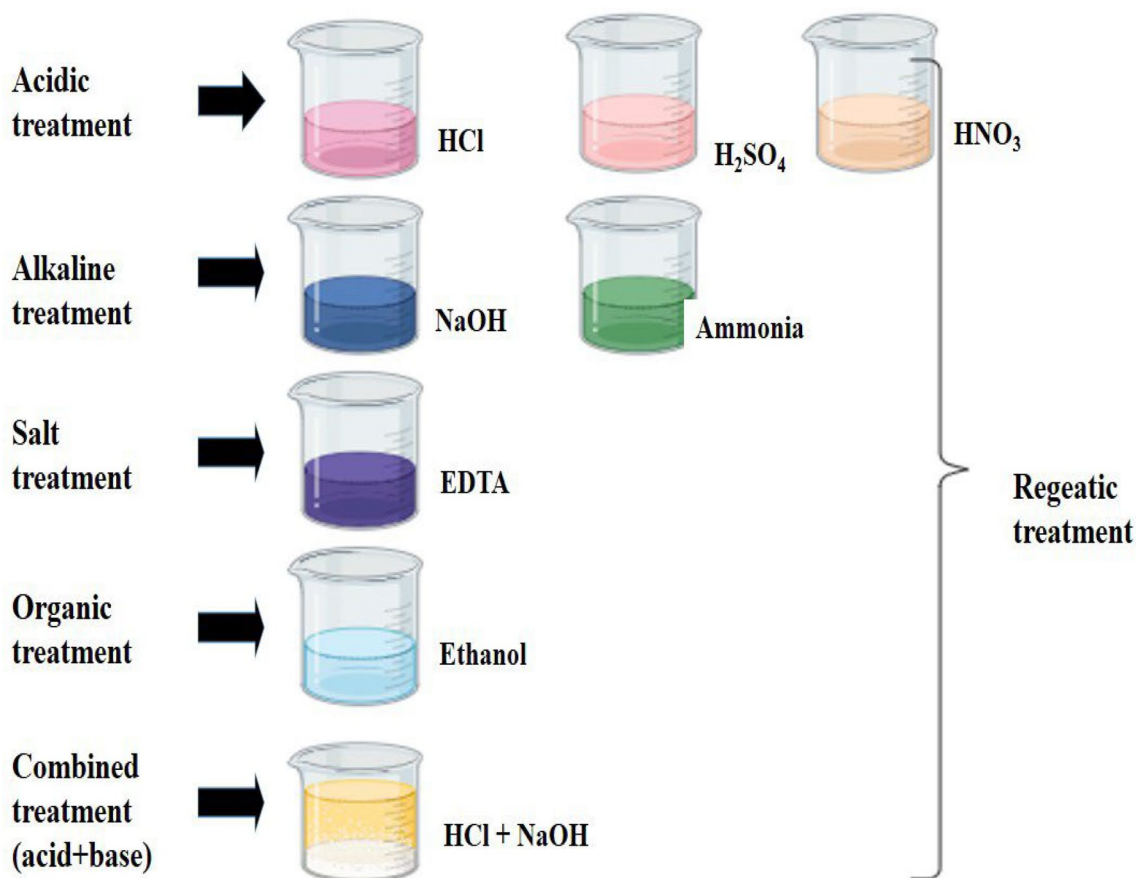


Fig. 12 Methods used for regeneration and reuse of modified biochar

Table 4 Regeneration and reuse of modified biochar

Biochar feedstock	Modifying agent	Desorbent	Heavy metal ions	Cycle times	References
Tieguanyin tea stalks	Potassium ferrate	HCl (0.1 M)	Zn(II), Cu(II)	5	[77]
Raw data leaves and stalks	Fe <sub>3</sub> O <sub>4</sub> nanoparticles	HCl (0.1 M)	Cd(II), Pb(II)	5	[102]
<i>Paeonia ostii</i> seed coats	Phosphoric acid	HCl (0.1 M)	Cu(II)	6	[107]
Water hyacinth	FeCl <sub>3</sub>	HNO <sub>3</sub> (0.1 M)	Cr(VI)	3	[108]
Glue residue	ZnCl <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> (0.1 M)	Cr(VI)	6	[82]
Saw dust	Graphene oxide	NaOH (0.01 N)	Cd(II)	5	[109]
Residue of maize hybrid	Fe <sub>3</sub> O <sub>4</sub>	NaOH (0.5 M)	Fe(II)	5	[110]
Dried loofah sponges	Chitosan, FeCl <sub>3</sub>	NaOH (0.1 M)	Cr(VI), Cu(II)	6	[99]
Water hyacinth	ZnO nanoparticles	Ammonia water (15%)	Cr(VI)	5	[111]
Saw dust	Molybdenum disulphide	EDTA (0.5 M)	Pb(II)	6	[79]
Macadamia nut shell	Carboxymethyl chitosan, potassium ferrate	EDTA (0.01 M)	Zn(II)	3	[105]
Rosin (a solid form of resin)	α-Fe <sub>2</sub> O <sub>3</sub>	HCl (1 M) and NaOH (1 M)	Cr(VI)	–	[112]

## 7 Conclusion

Heavy metal pollution effects every sphere of the ecosystem. Remediation of heavy metals from water is the major concern of today's era. In this regard, biochar, a carbon-rich adsorbent derived from biomass pyrolysis has received interest

in water remediation since it promotes sustainable practices such as circular economy and green chemistry. Biochar has good cation exchange capability and its low cost make it ideal for adsorbing heavy metals which also help achieve the SDG-6 goal: Clean Water and sanitation. A bibliometric analysis was done to examine published literature to quantify and evaluate research patterns such as publication counts, world cloud, keywords co-occurrence network, trends topic, and the contributions of different countries in this field.

The biochar prepared from agricultural waste have better specific surface area and porosity than the other feedstock. Agro waste-based biochar is also economical for large-scale production. However, biochar has limited functional groups and needs to be modified to improve its effectiveness. Studies indicate that physically, chemically, or biologically altering biochar can significantly enhance its adsorption properties. Among ball milling, steam activation, and gas filling approaches, ball milling technique is found most effective physical modification as it increase its pore volume, size, specific surface area, and functional groups. The chemical treatments with acids, bases, or metal oxides have better improved biochar functioning than physical activation. Metal oxide ( $\text{Fe}_3\text{O}_4$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$ ) enhances functional groups and active sites on biochar surfaces, which results in higher heavy metal removal affinity compared to other chemical modifications. However, impregnation of metal oxide with biochar should be done in a specific ratio as its higher concentration can decrease porosity. The biological alterations utilizing microorganisms like bacteria, fungi, or algae further boost its adsorption efficacy through ion exchange and surface grafting mechanism. The microbial inoculation and enzyme treatment release organic acids and proteins that enhance biochar efficiency for heavy metals. But the efficiency of biological activation is lower than chemical treatment. When biological modification accompany chemical activation, it results in a sustainable, green, adsorbent for heavy metals remediation.

The modified biochar can effectively remove heavy metals via physical adsorption,  $\pi$  interaction, complexation, surface precipitation, co-precipitation, electrostatic attraction, and ion exchange. A better knowledge of molecular-level adsorption mechanisms will be required, and technologies such as X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) can provide valuable insights into biochar-heavy metal interactions. Furthermore, examining more effective biochar regeneration technologies is critical for reducing costs and environmental impact, highlighting the need for additional investigation. Biochar's practical efficacy must also be evaluated in complex wastewater conditions where competing ions and organic debris can affect adsorption effectiveness. Life cycle assessments will assist in determining the environmental sustainability of biochar production, modification, and disposal. Scaling up biochar synthesis for industrial use will necessitate optimization and long-term research. The main key barriers for large scale production of biochar are cost of raw material and less advance pyrolysis unit in many regions. By using waste biomass (e.g. agricultural residues, forestry waste) as feedstock, adopting low energy pyrolysis techniques and government subsidies can promote biochar large scale production. Finally, combining biochar with other water treatment technologies, such as membrane filtration or sophisticated oxidation processes, may improve its efficacy, and more research should look into these synergies. By addressing these issues, biochar can become a long-term and feasible option for heavy metal remediation, resulting in cleaner water and a better ecosystem.

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## Declarations

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

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