# REVIEW



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# Engineered biochar for environmental decontamination in aquatic and soil systems: a review

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# Abstract

Contamination of aquatic and soil systems by organic and inorganic pollutants has become a serious issue of concern worldwide. Viable and cost-effective solutions are urgently needed to mitigate the negative impacts of diverse pollutants on the environment and human health. Biochar has emerged as an effective and green material for the remediation of a wide spectrum of (in)organic pollutants. However, applications of pristine biochar in decontamination have encountered bottlenecks due to its limited properties which cannot meet the desired remediation requirements. Therefore, multiple modification methods have been developed for tailoring the physicochemical properties of biochar to enhance its effectiveness in environmental decontamination. This work provides a holistic review on the recent advances on the synthesis of engineered biochar using physical, chemical, and biological methods. Further applications and related mechanisms of engineered biochar in the field of environmental decontamination in aquatic and soil systems have also been summarized and discussed. In addition, existing challenges and research gaps are outlined, and future research needs are proposed. This review summarizes the scientific opportunities for a comprehensive understanding of using engineered biochars as effective materials for the remediation of contaminated water and soil.

# Highlights

- Recent advances on biochar functionalization using physical, chemical, and biological methods are reviewed.
- Decontamination behaviors and mechanisms of (in)organic pollutants by engineered biochar are summarized.
- Existing knowledge gaps are identified, and outlooks of engineered biochar applications are proposed.

Keywords: Modified biochar, Heavy metal, Organic pollutant, Nutrient, Adsorption, Remediation

Graphical abstract

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## 1 Introduction

Rapid urbanization and industrialization together with anthropogenic activities have resulted in ecological disturbances (Monga et al. 2022). Environmental pollution caused by (in)organic pollutants is considered as one of the most urgent issues of recent times due to its alarming health risks to biota (Shaheen et al. 2022b), which requires sustainable remediation approaches. Decontamination techniques using carbonaceous materials such as activated carbon, carbon nanotubes, graphene, and biochar have been developed to minimize the contaminants' detrimental impacts on the environment (Hu et al. 2020; Kumar et al. 2020). Among them, biochar has several advantages. The estimated cost for biochar is around USD  $246 t^{-1}$ , which is about 1/6 of commercial activated carbon (Premarathna et al. 2019), and also far less than that of carbon nanotubes and graphene. Furthermore, the source of feedstock for biochar production is more flexible than the others. Considering the perspective of

economic and environmental sustainability, biochar is deemed as the most promising carbonaceous material for environmental applications. Biochar is a carbon-rich byproduct produced from a range of renewable biomass wastes under oxygen-limited conditions (Lehmann 2007). As a low-cost and sustainable material with high adsorption capacity and chemical stability, biochar is an effective and eco-friendly adsorbent for pollutant adsorption/immobilization (Shaheen et al. 2022a). For instance, investigations demonstrated that pig-carcass biochar effectively decreased the bioavailability of di-(2-ethylhexyl) phthalate (DEHP) and cadmium (Cd) in contaminated soils (Chen et al. 2019, 2020). Biochar is an appealing choice in the fields of waste management and environmental remediation, owing to its feasibility of large-scale production and multifunctional values (Bolan et al. 2022).

Although biochar has many advantages, the application of pristine biochar in environmental remediation has



encountered some bottlenecks: 1) low functionality, such as insufficient porosity and surface area (Kumar et al. 2020); 2) the challenge to separate fine biochar from soil/ water phase (Lyu et al. 2020a); 3) limited adsorption efficiency for contaminants at high concentrations (Ahmed et al. 2016); 4) weak affinity to toxic anionic species (e.g., Cr, As, and Sb) due to the negatively-charged surface nature (Chen et al. 2022b) and potential mobilization of oxyanionic contaminants at elevated pH conditions induced by biochar application (Shaheen et al. 2022a, 2022b); 5) potential release of biochar-carried dissolvable pollutants (e.g., metal(loid)s, polycyclic aromatic hydrocarbons (PAHs), persistent free radicals (PFRs) and volatile organic compounds (VOCs)) (Duan et al. 2019).

Consequently, various modification methods for tailoring the physicochemical properties of biochar have been applied to enhance its effectiveness in environmental applications. In general, functionalization methods for biochar can be categorized into three types, i.e., physical, chemical, and biological modifications (Zhang et al. 2022d), which are summarized in Fig. 1. Physical modification including steam/CO<sub>2</sub> activation, microwave activation, and ball milling alters the pore structure, particle size, surface area, and functional groups of biochar. It offers advantages over chemical methods such as clean and economically feasible biochar production (Duan et al. 2019). Chemical modification methods include acid-base modification, oxidizing treatment, magnetization, loading of clay minerals, carbon nanomaterials, layered double hydroxides, organic surfactants, and nonmetallic element doping, which not only affect the physical properties of biochar, but also significantly influence its chemical properties (e.g., elemental distribution, surface functional groups, point of zero charge, cation exchange capacity, and electron transfer capacity) (Chen et al. 2022b; Medeiros et al. 2022). Changes in the physicochemical properties of biochar affect its potential for environmental applications. Furthermore, biochar can be modified by the biological methods, which takes advantage of microorganisms and biological-related processes (Monga et al. 2022), and further aid in the removal of toxic pollutants.

There have been some reviews focusing on different applications of biochar including aqueous contaminant removal (Hu et al. 2020; Krasucka et al. 2021; Zhang et al. 2020a; Bolan et al. 2022; Medeiros et al. 2022), soil property improvement (Zhang et al. 2022d), soil fertility enhancement (Marcińczyk and Oleszczuk 2022) and catalysis (Monga et al. 2022). To date, most reviews focus more on using pristine and engineered biochar to remove contaminants from aqueous solutions (e.g., Shaheen et al. 2022b, 2022c), particularly the former. However, a holistic review including the applications of engineered biochar in the remediation of both aquatic and soil systems has rarely been reported. Moreover, the summarized information of emerging modification methods for biochar such as nonmetallic heteroatom doping is limited. Recently, Kasera et al. (2022) reviewed the nitrogendoped biochars as adsorbents in the removal of heavy metals and organics from water, yet biochar doped by other nonmetallic heteroatoms such as sulfur (S) and boron (B) was not well summarized till now. With the aim to provide a detailed overview of engineered biochar for environmental decontamination, based on the publications in recent years, especially in recent five years, this updated review thoroughly summarized the most recent advancements in emerging modification methods for biochar such as nonmetallic heteroatom doping, advanced characterization techniques for biochar analysis, and frontier applications of engineered biochar in both water and soil remediation while addressing pertinent mechanisms involved from multiple aspects. We also maximized the capacity of this review to cover more types of engineered biochar and contaminants to provide an exhaustive reference to the readers. In addition, existing challenges and research gaps are discussed, and future research needs are proposed.

## 2 Synthesis of engineered biochar

#### 2.1 Physical modification

In general, physical modification of biochar includes steam and microwave activation,  $CO_2$  purging, and ball milling, which are usually simpler and less expensive than chemical activation methods (Ahmed et al. 2016). Physical activation has been considered as an effective approach to enhance the biochar functionality by influencing biochar's properties (e.g., surface functional groups, polarity and hydrophobicity) (Medeiros et al. 2022). However, the drawbacks of physical modification methods include high energy consumption and long activation time (Shaheen et al. 2022b). For these reasons, chemical modification is considered to be the primary option for biochar modification. Future research should focus on filling the knowledge gap to address the disadvantages of physical modifications.

## 2.1.1 Steam/CO<sub>2</sub> activation

Steam activation can upgrade pristine biochar to activated biochar by increasing its porosity and surface area (Medeiros et al. 2022) and introducing oxygen-containing surface functional groups such as carbonyl and hydroxyl groups (Ahmed et al. 2016). There are two reasons for the increased porosity and surface area of resultant biochar after steam treatment: first, interaction of water vapor and labile organic matter of biomass to generate gas; second, consumption of carbon in the precursor (Anderson et al. 2021). Both reactions can reduce the formation of pore blocking tar and enlarge the pores of biochar. Steam activated biochar has shown superior performance in the removal of hazardous compounds, including metal(loid)s (Kwak et al. 2019; Yan and Li 2022); dyes (Yek et al. 2020), phosphate (Han et al. 2020; Wen et al. 2021b), antibiotics (Wang et al. 2020a) and landfill leachate (Yek et al. 2021). In addition, steam-activated biochar also facilitated the stabilization of polyfluoroalkyl substances (PFAS) (Sørmo et al. 2021) and carbamate pesticides (Tang et al. 2021) in the soil. However, Shim et al's research reported that Miscanthus derived biochar after steam activation showed a negligible influence on Cu removal, which might be ascribed to the steam activation-induced degradation of functional groups (e.g., -OH, C=O) of biochar and thus weakened the complexation effect (Shim et al. 2015). In practice, other modification methods such as microwave modification (Yek et al. 2020, 2021) and magnetization (Han et al. 2020; Wen et al. 2021b) were applied in parallel with steam activation to obtain a higher adsorption capacity of biochar, which are briefly discussed below.

Biochar tailoring can also be carried out by employing  $CO_2$  as an activation gas, which facilitates the formation of microporous structure of biochar (Medeiros et al. 2022). Purging  $CO_2$  during pyrolysis has shown favorable effects on the production of biochar with high porosity from barley straw (Pallarés et al. 2018), orange peel (Yek et al. 2020), rice straw and sludge (Islam et al. 2021), and waste timber (Sørmo et al. 2021). Pallarés et al. (2018) reported that barley straw-derived biochar produced in  $CO_2$  condition displayed a large surface area, up to nearly 800 m<sup>2</sup> g<sup>-1</sup>. Moreover, CO<sub>2</sub>-activated biochar exhibited its effective performance in environmental decontamination. For instance, Islam et al. (2021) demonstrated good adsorption efficiency of CO2-activated biochar derived from paper mill sludge for various heavy metals, including  $Cu^{2+}$  (39.4 mg g<sup>-1</sup>),  $Cd^{2+}$  (30.0 mg g<sup>-1</sup>), and  $Pb^{2+}$  $(250 \,\mathrm{mg}\,\mathrm{g}^{-1}).$ 

#### 2.1.2 Microwave activation

Microwave activation is an advanced technique based on high-frequency electromagnetic irradiation with frequencies ranging from 0.03 to 300 GHz (Duan et al. 2019). Microwave radiation induces dipole rotation at an atomic scale, thus generating heat energy within the materials (Yek et al. 2020). This modification method allows both inner and outer surfaces of biochar to be heated simultaneously without direct contact at a low temperature of 200–300 °C (Zhou et al. 2021b), and renders microwave-activated biochar with more functional groups and higher surface area as compared to the pristine biochar (Zhang et al. 2022c). In a study, Kołtowski et al. (2017) reported that microwave-activated biochar was more effective on decreasing the phytotoxicity of heavy metals (e.g., Pb, Cr, Cu, Cd) and PAHs in Lepidium sativum compared to raw biochar. Additionally, microwave activation for biochar also promoted the removal of methylene blue (Yek et al. 2019) and Congo red (Yek et al. 2020) from wastewater. As an example, Yek et al. (2019) reported that the combined application of microwave and steam activation produced high-grade activated biochar with a high surface area of 571 m<sup>2</sup> g<sup>-1</sup>, and resulted in an effective performance in the removal of methylene blue with maximum adsorption capacity of  $38.5 \,\mathrm{mg g}^{-1}$ . However, the environmental application of microwave-activated biochar is still limited, which is mainly attributed to the high cost of equipment operation and maintenance (Foong et al. 2020).

## 2.1.3 Ball milling

Ball milling, an eco-friendly and low-cost approach, has been employed for the modification of biochar via improvement of specific surface area (SSA) and pore structure (Cheng et al. 2021b), and enrichment of surface functional groups, as compared to the non-activated biochar (Lyu et al. 2018; Xiao et al. 2020). Ball-milling technique mechanically adjusts the particle size to the nanoscale (<1000 nm) under non-equilibrium conditions (Lyu et al. 2020b). Previous studies have reported that various operational parameters could affect the physicochemical and adsorptive/catalytic properties of resultant biochar, including mass ratio of media: biochar, wet or dry milling (with or without solvent), solvent properties, reaction time, milling speed, milling temperature, ball size distribution, and reaction atmosphere (Lyu et al. 2018; Huang et al. 2020a; Xu et al. 2021; Zhao et al. 2022). In addition, the shape of grinding media (spherical balls, ellipsoids, and cubes) may influence the milling process, and spherical balls are the best grinding media, as indicated by Simba and Moys (2014). Ball-milled biochar in the remediation of inorganic pollutants has been studied in recent years. For instance, Cui et al. (2021b) confirmed that the ball milling method facilitated the incorporation of Mg/Al layered double hydroxide (LDH) into biochar matrix, and the ball-milled Mg/Al LDH-biochar composite showed a very high adsorption capacity for Cd(II)  $(119 \text{ mgg}^{-1})$ . In addition to metal(loid)s, ball-milled biochar has also shown great potential for the removal of other inorganic pollutants such as ammonia (Qin et al. 2020), phosphate (Feng et al. 2022; Li et al. 2022a), and various organic contaminants such as antibiotics (Huang et al. 2020a), dyes (Luo et al. 2022), phenols (Zhao et al. 2022), etc. Additionally, emerging applications using ball-milled biochars have focused on photo/thermal cataly-sis (Xiao et al. 2020) and soil remediation (Zhang et al. 2022a, 2022b). Although ball-milling technique is a new field of research to synthesize engineered biochar, it is still in its infancy. Therefore, further research is needed to determine crucial research directions and overcome the existing challenges.

## 2.2 Chemical modification

## 2.2.1 Acid, alkaline, and oxidant modifications

For acid treatment, removal of impurities such as metals on biochar is the main purpose, in which the acidic functional groups such as phenolic, carboxylic, and lactonic groups are also introduced (Wang and Wang 2019; Zhou et al. 2021b). The commonly used acids for biochar modification included nitric acid (HNO<sub>3</sub>), hydrochloric acid (HCl), sulfuric acid ( $H_2SO_4$ ), phosphoric acid ( $H_3PO_4$ ), citric acid ( $C_5H_8O_7$ ), and oxalic acid ( $C_2H_2O_4$ ) (Medeiros et al. 2022). Acid modification can decrease the alkalinity of biochar, thus the biochar with lower pH might show a potential prospect for remediation of alkaline calcareous soil (Zhou et al. 2021b). On the other hand, base activation also significantly affects the biochar properties, causing higher aromaticity and N/C ratio, but a lower O/C ratio of biochar compared to acid modification (Ahmed et al. 2016). Potassium hydroxide (KOH) and sodium hydroxide (NaOH) are the commonly used bases (Duan et al. 2019). The alkaline treatment can cause a decrease in the acidic oxygen-containing functional groups such as C=O, while enriching the hydroxyl groups (Yao et al. 2020). In addition to acid/alkaline modification, biochar can also be modified using oxidizing agents such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), potassium permanganate  $(KMnO_4)$ , and ozone  $(O_3)$  (Yuan et al. 2019). The oxidantmodified biochar has high thermal stability in remediation applications and large affinity to bind pollutants (Zhou et al. 2021b). For instance, KMnO<sub>4</sub>-modified biochar removed >97% of sulfamethoxazole within 30 min (Tian et al. 2019). Most studies have reported that modified biochars using acid/alkaline/oxidant improved surface properties of biochar and consequently enhanced the removal of metal(loid)s and organic contaminants in aqueous system (Cheng et al. 2021b; Medeiros et al. 2022). However, some researchers have reported that the above-mentioned modifications showed negative effects on pollutant removal. For example, pinewood biochar modified by 10% H<sub>2</sub>O<sub>2</sub> caused a decrease of adsorption capacity for methylene blue compared to pristine biochar, which is likely attributed to the weakening of  $\pi$ - $\pi$  dispersive forces caused by the introduction of oxygen functionality (Huff and Lee 2016).

### 2.2.2 Iron modification

Iron (Fe) modification method for biochar is proposed for two main objectives: i) reinforcing the separation efficiency to recycle and reuse the biochar (Huang et al. 2019b); ii) enhancing the decontamination capacity of biochar via the interaction between the loaded Fe and target contaminants (Wen et al. 2021a). Iron-modified biochar has been developed using iron oxides (e.g., hematite and goethite), iron sulfide (FeS), and nano zero-valent iron (nZVI) (Lyu et al. 2020a). Iron-modified biochar can be synthesized via co-pyrolysis (Yang et al. 2022a), precipitation (Yang et al. 2022b), thermal reduction (Wang et al. 2019a), and ball milling methods (Kumar et al. 2020), which can be classified into "pre-treatment of biomass" and "post-treatment of iron materials" (Huang et al. 2019b). Considering previous publications, the application of Fe-modified biochar can be divided into three types, i.e., an adsorption material, a reductive agent, and a catalyst.

Goethite ( $\alpha$ -FeOOH) and hematite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) are the most commonly used Fe minerals to enhance the biochar's adsorption efficiency for metal(loid)s, including Cd, Pb, Cu, Cr, As, and Hg (Lyu et al. 2020a). Zhu et al. (2020) synthesized an  $\alpha$ -FeOOH modified wheat straw biochar ( $\alpha$ -FeOOH@BC) and its maximum adsorption capacities for Cd(II) and As(III) were 63 mg g<sup>-1</sup> and 78 mg g<sup>-1</sup>, respectively. Shan et al. (2016) prepared three types of Fe-modified biochars, i.e., Fe-biochar, Fe<sub>2</sub>O<sub>3</sub>-biochar, and Fe<sub>3</sub>O<sub>4</sub>-biochar through one-step ball milling of iron powder (Fe), ferric oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>), respectively. In the removal trial for pharmaceutical compounds, Fe<sub>3</sub>O<sub>4</sub>-biochar displayed the highest adsorption capacities for carbamazepine (63 mg g<sup>-1</sup>) and tetracycline (94 mg g<sup>-1</sup>).

Iron-modified biochar has also shown great performance in the redox reactions of metal(loid)s (e.g., As(III), Cr(VI) and U(VI)) and organic contaminants to minimize their toxicity (Yuan et al. 2017; Feng et al. 2021; Amen et al. 2020; Zhu et al. 2022). Biochars modified by nZVI, FeS, and FeOOH have been investigated for reductive degradation since they can provide reductive agents (e.g., Fe<sup>0</sup>, S(II), and Fe(II) species). Zhu et al. (2022) found that the nZVI modified biochar showed effective adsorption for Cr(VI) (54.4 mgg<sup>-1</sup>). The reduction of toxic Cr(VI) to less toxic Cr(III) was also noted, which highlighted the vital role of Fe<sup>0</sup>. The superiority of nZVI modified biochar over pristine biochar or nZVI alone was confirmed for the removal of sulfamethazine, because nZVI modified biochar facilitated the generation of free radicals (•OH) which favored the degradation of sulfamethazine (Deng et al. 2018). Liu et al. (2021a) reported that peanut shell biochar modified by FeS and starch reduced labile U(VI) to non-labile U(IV) species, and the key role of Fe<sup>0</sup> and S(II) in the reduction process was highlighted by XPS analysis.

Another important direction for the application of Fe-modified biochar is in the degradation of organic pollutants (Feng et al. 2021), particularly in Fenton-like and persulfate activation systems. Activation of oxidants (e.g.,  $H_2O_2$ , persulfate, permanganate, and ozone) by Fe-modified biochar has received extensive attention (Lyu et al. 2020a). Owing to high electron shuttling capacity, abundant PFRs and oxygen-containing functional groups, Fe-modified biochar has been verified for its potential as a Fenton-like catalyst in catalyzing H<sub>2</sub>O<sub>2</sub> to form hydroxyl radicals (•OH) to eliminate organic contaminants in aquatic solution (Feng et al. 2021). When Fe-modified biochar is applied in the Fenton-like system,  $Fe^0$  can be oxidized to  $Fe^{2+}$  (Eqs. (1), (2)) and  $Fe^{3+}$  can be reduced to  $Fe^{2+}$  (Eqs. (3), (4)), and •OH is finally generated through Eqs. (5) to degrade organic contaminants (Feng et al. 2021).

$$2Fe^{0} + O_{2} + 2H_{2}O \rightarrow 2Fe^{2+} + 4OH^{-}$$
(1)

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2$$
 (2)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2 \bullet$$
 (3)

$$Fe^{3+} + HO_2 \bullet \to Fe^{2+} + H^+ + O_2$$
 (4)

$$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \to \mathrm{Fe}^{3+} + \mathrm{OH}^- + \bullet\mathrm{OH}$$
 (5)

In addition,  $Fe^{2+}$ , PFRs on Fe-modified biochar can function as effective activators to generate reactive oxygen species (ROS) (e.g., •OH,  ${}^{1}O_{2}$  and  $SO_{4}$ •<sup>-</sup>), which can effectively degrade a variety of organic pollutants such as tetracycline (Luo et al. 2021), bisphenol A (Jiang et al. 2019), metronidazole (Yi et al. 2019), and phthalate esters (Dong et al. 2020). For instance, with the aid of ESR analysis, Yi et al. (2019) confirmed that the addition of magnetic sugarcane bagasse-derived biochar favored the generation of ROS in a Fenton-like system, and •OH radical quenching experiments showed that the removal efficiency decreased by approximately 85%, highlighting the dominating role of •OH in the degradation of metronidazole. Moreover, iron modification can result in a narrower band gap of biochar, which aids the adsorption/photocatalysis for aqueous Cr(VI),  $Pb^{2+}$ ,  $F^-$  and methylene blue (Herath et al. 2022).

Compared to other metal oxides and metal salts, iron is the most abundant element on the earth, more costeffective, and less environmentally risky. Therefore, Femodified biochar is recommended as an amendment in the remediation of contaminated soil system due to such advantages. Iron modification has been the most widely developed and practical tailoring technique in the remediation of environmental contaminants by biochar at large-scale applications.

## 2.2.3 Metal oxides and metal salts

Loading of metal oxide and metal salt onto biochar can enhance the adsorption efficiency of biochar by introducing different functional sites. The most commonly used metal, Fe, has been thoroughly discussed in Section 2.2.2. Second to Fe, manganese (Mn) has also been widely applied due to the advantages including abundant earth resources, ease of operation and environmental friendliness (Shaheen et al. 2022b). A series of Mn-coated biochars with different Mn:biochar mass ratios were prepared using  $MnSO_4 \cdot H_2O$  as the modifying agent by Jia et al. (2020). The maximum adsorption capacities for Sb(III) and Sb(V) by Mn-coated biochar were 0.9 and  $0.7 \text{ mgg}^{-1}$ , respectively (Jia et al. 2020). Moreover, Mnmodified biochar also showed nearly 100% removal of 4-chloro-3-methyl phenol (CMP) in persulfate activation system, and enhanced catalytic performance was ascribed to the generated  $SO_4^{\bullet-}$ ,  $\bullet OH$ , and  $^1O_2$ , which facilitated the CMP degradation (Liu et al. 2021b). Other metals for biochar modification include magnesium (Mg) (Zheng et al. 2020), aluminum (Al) (Wang and Wang 2019), copper (Cu) (Zhong et al. 2020), cerium (Ce) (Dong et al. 2020), lanthanum (La) (Wang et al. 2018), zirconium (Zr) (Rahman et al. 2021), bismuth (Bi) (Zhu et al. 2019), etc. Advanced progress has been achieved in the functionalization of biochar using metal oxides, metal salts, and even metal monoatoms (e.g., cobalt (Co)). In a recent study, a novel biochar based-N, S-anchored single-atom catalyst was developed by Cui et al. (2021a). The authors confirmed an atomic dispersion of Co throughout the coffee grounds-derived biochar, and it demonstrated high degradation efficiency of 90–100% for diethyl phthalate (DEP) and bisphenol A in the peroxymonosulfate activation system.

## 2.2.4 Nonmetallic heteroatom doping

Nonmetallic heteroatom doping is an emerging technique to functionalize biochar by regulating its electronic properties, thus enhancing its adsorptive/catalytic capacity for pollutant removal (Baser et al. 2021). Previous researches, involving nonmetallic element doped biochar and associated environmental applications and mechanisms, are summarized in the Supplementary Materials (Table S1). As demonstrated, the most commonly used nonmetallic elements for biochar modification include nitrogen (N), sulfur (S), and boron (B). Additionally, biochar doped with phosphorus (P) (Pan et al. 2022) and iodine (I) (Wang et al. 2021) was also reported to remove aqueous contaminants.

Nitrogen is the most intensively explored heteroatom in biochar doping (Baser et al. 2021). The N-doping method can improve the electrochemical performance of biochar via forming graphitic N, pyrrolic N, pyridinic N, and amine-N species during the doping process (Leng et al. 2020; Kumar et al. 2022). The graphitic-N can promote electron transfer within the carbon skeleton, thus improving the catalytic performance of N-doped biochar for persulfate activation (Baser et al. 2021). The pyrrolic N and pyridinic N bonds can act as electron donors, and simultaneously generate N defects which provide additional active sites in N-doped biochar (Zhang et al. 2021a). The amine-N group can act as the binding site for metal(loid)s ions via the chelation effect (Chen et al. 2022b). Therefore, N-doped biochar has been applied as an effective adsorbent/catalyst in the removal of antibiotics, phenols, dyes, and heavy metals, etc. (Table S1). For instance, Cheng et al. (2021a) synthesized N-doped biochar derived from alfalfa and it showed significant adsorption capacity for methylene blue  $(326.90 \text{ mgg}^{-1})$ and methyl orange (906.52 mgg $^{-1}$ ). Spectroscopic analyses and theoretical calculations confirmed that the introduced pyrrole N and pyridine N played decisive roles in the removal of both dyes, and the proposed mechanisms included  $\pi$ - $\pi$  stacking, electrostatic interactions, and hydrogen-bonding (Cheng et al. 2021a). More importantly, N-doped biochar showed great potential in the catalytic performance for pollutant removal. For example, Wang and Chen (2022) reported that the optimized N-doped biochar displayed high surface area  $(738 \text{ m}^2 \text{g}^{-1})$ and N content (13.5%), and this biochar showed great catalytic performance for peroxymonosulfate activation to remove sulfamethoxazole, with a removal rate of 95% within 30 min. As revealed by the quenching tests and EPR spectra, the singlet oxygen  $({}^{1}O_{2})$  was found to be the dominating reactive species contributing to the degradation of sulfamethoxazole, and the nonradical oxidation involving  ${}^1\mathrm{O}_2$  and electron transfer were the main removal mechanisms.

Other than nitrogen, heteroatom like S can also be used for doping the biochar. Sulfur doping endows biochar with more functional groups such as C–S, C–S–C, C=S, C–S–O, and sulfur rings (Zhang et al. 2021a; Wan et al. 2022). Specifically, C–S–C groups can strengthen the spin density of surrounding carbon atoms, thus

improving the catalytic activity of biochar (Liu et al. 2020). Furthermore, C-S-O structure in the biochar can induce nucleophilic addition of peroxymonosulfate to generate abundant singlet oxygen  $({}^{1}O_{2})$  (Wan et al. 2022). Biochar after S-doping has shown a high affinity towards (in)organic compounds. For instance, Yang et al. (2019) first fabricated a hierarchical cornstraw biochar/Fe composite, then S<sup>2-</sup> and Mn<sup>2+</sup> were simultaneously introduced, forming a ternary ironmanganese-sulfur/biochar composite. This composite was tested to remove aqueous Pb(II), and the authors concluded that the S doping enhanced Pb removal via precipitation of PbS. Another study showed that S-doping could introduce phenoxyl radicals such as C-O<sup>•</sup> and vacancy defects on the wood-waste biochar, which facilitated the activation of peroxymonosulfate to degrade 91% of bisphenol A in 30 min (Wan et al. 2022). Scavenging experiments and Raman analyses verified that the S-doped biochar triggered the generation of surface-bound  ${}^{1}O_{2}$  (major) and •OH (minor), which contributed to the effective removal of bisphenol A.

Boron is another ideal candidate heteroatom which can modulate electron distribution and tailor the physicochemical properties of biochar, and further provide more defect sites (Sui et al. 2021). Boron-doping increased the specific surface area (up to 898 m<sup>2</sup> g<sup>-1</sup>) and increased oxygen-containing functional groups of corn-straw biochar, which ultimately enhanced its ability to adsorb Fe(II) (Sui et al. 2021). The interaction mechanisms between Fe(II) and B-doped biochar involved chemical complexation, ion exchange, and co-precipitation. Regarding the catalytic effect of B-doped biochar, Liu et al. (2020) used the B-doped wheat straw biochar to activate peroxydisulfate (PDS) for the removal of sulfamethoxazole, and a superior degradation of sulfamethoxazole (94%) was observed in 120 min. Experimental and theoretical results elucidated that the introduced B species could act as Lewis acid sites to enhance the surface affinity towards PDS and that the biochar mediated electron transfer mechanism was majorly responsible for the nonradical route.

Furthermore, many studies have explored the co-doping of two substances on biochar. Nitrogen and copper co-doped biochar prepared by Zhong et al. (2020) was used to degrade tetracycline, and the co-doped biochar displayed improved performance compared to N-doped biochar or Cu-doped biochar. Zhang et al. (2022e) fabricated three types of doped biochars, i.e., N-doped (N-BC), S-doped (S-BC), and N and S co-doped (NS-BC) biochar derived from moso bamboo. However, they found that the degradation rate of antibiotics by NS-BC (71%) was lower than that of N-BC (92%) and S-BC (89%). The main reason for this phenomenon was that NBC had the highest concentration of persistent free radicals (i.e.,  $SO_4$ •<sup>-</sup> and •OH), larger specific surface area and higher defects.

Although considerable advances in the non-metal elements-doped biochar have been achieved, it still is an emerging direction due to its huge potential for improvement in environmental remediation. The non-radical mechanism behind persulfate activation is still ambiguous, which needs to be further explored. In addition, the complex sample preparation, high cost, and poor reusability of this type of biochar need to be properly addressed in future research.

## 2.2.5 Clay minerals

Natural clay minerals including montmorillonite, vermiculite, zeolite, kaolinite, and illite are easy to mine, highly abundant, inexpensive, and nontoxic geo-materials (Arif et al. 2021). They have been effectively used as adsorbents in the remediation of various contaminants (Feizi et al. 2019; Han et al. 2019). However, clay minerals have few drawbacks such as small particle size and poor flowability, and hence using them in combination with biochar to produce composite materials is a feasible option to take advantage of both resource materials. The introduction of clay minerals to biochar could increase the porosity and cation exchange capacity of biochar-clay composites, and also improve the adsorption capacity to heavy metals, antibiotics, and polymers, etc. (Premarathna et al. 2019). For instance, Fu et al. (2020) used montmorillonite-corncob biochar composites for Pb(II) removal from wastewater, which showed a significant adsorption capacity for Pb(II), up to  $140 \text{ mgg}^{-1}$ . Illite-modified biochar (IBC) with a 1:4 ratio of illite and walnut shell biochar was fabricated by Liu et al. (2022), and it showed effective removal of metolachlor from soil. The Langmuir-derived Qe value for IBC was higher than that of raw biochar ( $92 \text{ mgg}^{-1} \text{ vs } 73 \text{ mgg}^{-1}$ ).

## 2.2.6 Layer double hydroxides (LDHs)

Layered double hydroxides (LDHs) are robust adsorbents with layered stacking 3R structure, showing strong anion exchange capacity (Chen et al. 2022c). However, the adsorption performance of LDHs may also be limited by their dense, layered stack structure (Lyu et al. 2021). LDH-engineered biochar has been reported as superior adsorbent to maximize the effectiveness of both materials in the removal of different pollutants (Huang et al. 2019a; Ma et al. 2021a; Lartey-Young and Ma 2022). Lartey-Young and Ma (2022) synthesized a ternary Cu/ Zn/Fe LDH engineered biochar derived from bamboo, and this engineered biochar possessed efficient adsorption capacity for atrazine  $(63.64-87.04 \text{ mg g}^{-1})$ . In another study, compared to the raw biochar, Mg/Fe-LDH engineered biochar also showed enhanced performance in the catalytic degradation of sulfamethoxazole (Chen et al. 2022c). Batch adsorption experiments revealed that the Mg/Fe-LDH engineered biochar could activate urea-hydrogen peroxide to generate •OH, thus enabling enhanced degradation of sulfamethoxazole (91%). In addition to the application in aqueous solutions, LDHengineered biochar has exhibited its potential in the remediation of contaminated soils. For instance, Lyu et al. (2021) applied Mg/Al LDH-biochar composite to the soil contaminated by uranium (U) ( $\approx 1000 \,\mathrm{mg \, kg^{-1}}$ ), and results indicated that biochar-LDH treatment significantly decreased the cumulative U loss by 53%, and leaching concentration by 54%, compared to the control.

#### 2.2.7 Carbon nanomaterials

Carbon nanomaterials including graphene, graphene oxide, carbon nanotubes, and graphitic carbon nitride are the commonly used agents to synthesize modified composites (Zheng et al. 2019; Zhang et al. 2020a). These carbon nanomaterials possess a strong affinity to various pollutants, so biochar loaded with carbon nanomaterials has been widely studied to further achieve higher adsorption capacities for different toxic pollutants. Abdul et al. (2017) loaded graphene oxide onto wood biomass biochar and investigated its performance for dimethyl phthalate (DMP) removal. The results indicated that biochar-graphene composite had higher adsorption capacities for DMP ( $45.65 \text{ mgg}^{-1}$ ) via  $\pi$ - $\pi$  interaction and hydrophobic effect.

## 2.2.8 Organic surfactants

Recent studies have explored the environmental remediation using biochar modified with organic surfactants, such as chitosan (Chen et al. 2022b), pyromellitic dianhydride (PMDA) (Deng et al. 2017), acrylonitrile (Luo et al. 2018b), polyethyleneimine (PEI) (Li et al. 2020b), rhamnolipid (Zhen et al. 2021), phytic acid (Hua et al. 2022), and cetyltrimethylammonium bromide (CTAB) (Murad et al. 2022). For example, CTAB was employed as a cationic surfactant to enhance the positive charge on the surface of peanut-shell biochar. Adsorption experiments confirmed that the resultant CTAB-engineered biochar showed higher Cr(VI) removal efficiency (79%) than the pristine biochar (37%). Furthermore, its application to soil also significantly decreased the concentration of soilavailable Cr(VI) by 92%, compared to the control.

## 2.3 Biological modification

Compared to physical and chemical modification methods, biological methods for biochar tailoring are less studied, mainly due to their more complex operation characteristics. Initially, researchers used anaerobic bacteria to convert biomass into biogas and used the resulting digested residue for the synthesis of biochar (Yao et al. 2011). Biochar derived from anaerobically digested biomass residues often exhibits high pH, large specific surface area, strong ion exchange capacity and other excellent properties (Kumar et al. 2022), and has shown superior removal efficiency for phosphate (Yao et al. 2011) and heavy metals (Ngambia et al. 2019).

Moreover, a comparatively new approach using the biological post-treatment method to immobilize the microorganisms on biochar has gained recent attention. Biochar has been recommended as an excellent carrier for microbial inoculation, owing to high porosity, costeffectiveness, richness of nutrients, and simple preparation (Zhou et al. 2021b). Biofilm theory suggests that living cells can secrete a variety of polymers and anchor themselves onto the biochar surface, forming a microbial biofilm surrounded by an extracellular matrix, which facilitates the adsorption/degradation of pollutants (Lin et al. 2021; Zheng et al. 2021; An et al. 2022). A recent study by Zhang and Wang et al. (2021) investigated the removal potential of Bacillus cereus immobilized biochars produced from Chinese medicine residues for chlortetracycline. The maximum removal rate of chlortetracycline was up to 85%. Microbial inactivation test revealed that the removal mechanism of chlortetracycline was majorly governed by microbial degradation and physical/chemical adsorption by biochar (Zhang and Wang 2021). Enhanced bioremediation of diesel oil was reported by Zhou et al. (2021a), who used Vibrio sp. LQ2-immobilized biochar to treat the diesel oil-contaminated seawater. In addition to the aqueous phase, Qi et al. (2021) confirmed that biochar loaded with three strains (i.e., Bacillus subtilis, Bacillus cereus, and Citrobacter sp.) could effectively immobilize U(VI) and Cd(II) in the contaminated soil. Specifically, compared to the control, the concentration of DTPA-extractable U and Cd in the soil decreased by 69% and 56%, respectively, and bacterialoaded biochar reduced metal uptake thus promoted celery growth.

### 3 Characterization of engineered biochar

Detailed characterization of engineered biochar is the prerequisite to understand its physicochemical properties and adequately decipher the underlying mechanisms controlling biochar-contaminant interactions. The commonly adopted analytical techniques of biochar can be mainly classified as chemical and spectroscopic analysis (Fig. 2).

Chemical characterization including pH, ash content, surface alkalinity, cation exchange capacity (CEC),



elemental composition of biochar, Boehm titration for functional groups, etc. can be measured using traditional techniques used for other environmental samples such as soil with appropriate modifications (Bolan et al. 2022). Conventional and emerging spectroscopic analytical techniques include Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectrometry (EDS), Fourier transform infrared spectrometry (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), solid state nuclear magnetic resonance (NMR), electron spin/paramagnetic resonance (ESR/ EPR), magnetic hysteresis loop analysis, and mediated electrochemical reduction/oxidation (MER/MEO) analyses. In addition to the above-mentioned characterization methods, synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy (extended X-ray absorption fine structure spectrum (EXAFS) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy), and micro-X-ray fluorescence (µ-XRF) spectroscopy have been applied to detect the presence, atomic structure, and detailed speciation of metal(loid)s within biochar (Li et al. 2020a; Yang et al. 2022b). The specific roles of above-mentioned analytical techniques for biochar are illustrated in the Supplementary Material (Text S1). The combination of various analytical techniques allows us to further understand the morphological structure of biochar and underlying decontamination mechanisms.

## 4 Engineered biochar for environmental decontamination and related mechanisms

## 4.1 Aquatic systems

## 4.1.1 Metal(loid)s

Adsorption of metal(loid)s using various engineered biochars has been widely studied, and related adsorption efficiencies and associated mechanisms are summarized in Table 1. In general, the diversity of adsorption efficiency is governed by activation methods, original feedstocks, pyrolysis conditions, and target pollutants. The proposed metal(loid)s adsorption mechanisms by biochar involve pore filling, electrostatic effect,  $\pi$ - $\pi$  interactions, H-bonding, ion exchange, complexation, precipitation, and redox (Kumar et al. 2022; Shaheen et al. 2022b, 2022c). Figure 3 presents a summary of proposed removal/immobilization mechanisms for metal(loid)s by engineered biochar.

# Table 1 Metal(loid)s removal and associated mechanisms by engineered biochars in aqueous system

Feedstock	Pyrolysis conditions	Modification method	Metal(loid)s	Removal efficiency or capacity	Mechanisms involved	References
Canola straw	700 °C, 2 h	Steam activation	Pb(II)	195 mg g <sup>-1</sup>	lon exchange capac- ity, precipitation, and inner-sphere complexation.	Kwak et al. 2019
Poplar wood chip	300°C, 2h	Ball milling	Hg(II)	320 mg g <sup>-1</sup>	Surface adsorp- tion, electrostatic attraction, ligand exchange, and sur- face complexation.	Lyu et al. 2020b
Dendro	700 °C, —	Ball milling	Cr(VI) Cd(II)	7.46 mg g <sup>-1</sup> 922 mg g <sup>-1</sup>	Surface complexa- tion and electrostatic attraction.	Ramanayaka et al. 2020
Bamboo powder	700°C, 2h	Chitosan, Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> and FeSO <sub>4</sub>	Cr(VI)	127 mg g <sup>-1</sup>	Complexation, chelation, reduction, and electrostatic attraction.	Zhang et al. 2020b
Seaweed	200°C, 10 min	КОН	V(V)	12.3 mg g <sup>-1</sup>	Pore diffusion, elec- trostatic interaction, and complexation.	Ghanim et al. 2020
<i>Ficus</i> <i>microcarpa</i> aerial root	600 °C, 2 h	KMnO <sub>4</sub>	U(VI)	27.29 mg g <sup>-1</sup>	Surface adsorp- tion, electrostatic attraction, and O=U(VI)=O compl- exation.	Li et al. 2019
Corn straw	600 °C, 2 h	N-doping	Cu(II) Cd(II)	104.3 mg g <sup>-1</sup> 197.8 mg g <sup>-1</sup>	Cation-π bonding, complexation with graphitic-N, and hydroxyl groups.	Yu et al. 2018
Corn straw	800°C, 2 h	S-doping	Fe(II)	50.0 mg g <sup>-1</sup>	Chemical complexa- tion, ion exchange, and co-precipitation.	Sui et al. 2021
Glucose	800°C, 2 h	KOH and N doping	Cr(VI)	402.9 mg g <sup>-1</sup>	Physisorption, complexation, and reduction.	Liang et al. 2020
Populus L.	600°C,2h	FeCl <sub>3</sub>	As(III) As(V)	87.1% 99.2%	Physical adsorption, Fe–As precipitation, electrostatic interac- tion, and As(III) oxidation	Xu et al. 2020
Rapeseed straw	_	MnSO₄	Sb(III) Sb(V)	0.94 mg g <sup>-1</sup> 0.73 mg g <sup>-1</sup>	Physical adsorption, Sb–O–Mn complex, carboxyl/hydroxyl- Sb inner-sphere complexation, and electrostatic interac- tions.	Jia et al. 2020
Ficus microcarpa branch	500 °C, 2 h	Chitosan	Sb(III)	86–168 mg g <sup>-1</sup>	Electrostatic interac- tion, chelation, surface complexa- tion, $\pi$ - $\pi$ interaction, and H-bonding.	Chen et al. 2022b
Pork bone	500°C, 2 h	Cellulose	Pb(II)	115.7 mg g <sup>-1</sup>	Precipitation, ion exchange, and H– bonding.	Wang and Luo 2020
Pine wood	900°C, 1 h	Fe(NO <sub>3</sub> ) <sub>3</sub> and gra- phene assisted with steam activation	Pb(II)	153.2 mg g <sup>-1</sup>	Precipitation, compl- exation, and cation exchange.	Yan and Li 2022
Rice straw	400°C, 1 h	HCl and β-cyclodextrin	Pb(II)	131 mgg <sup>-1</sup>	Physisorption, ion exchange, and complexation.	Zhao et al. 2019

Feedstock	Pyrolysis conditions	Modification method	Metal(loid)s	Removal efficiency or capacity	Mechanisms involved	References
Undaria pinnatifida root	180°C, 24h	Hydroxyapatite	Cd(II)	99 mg g <sup>-1</sup>	Cation exchange, inner-sphere, and complexation.	Jung et al. 2019
Biosolid biomass	300 °C, 0.5 h	ZrCl <sub>4</sub>	As(V)	33.1 mg g <sup>-1</sup>	lonic attraction, precipitation, surface complexa- tion with Zr–O sites, hydrogen-bonding, and physical adsorp- tion.	Rahman et al. 2021
Phragmites australis	600 ℃, 25 min	LaCl <sub>3</sub>	Sb(V)	18.92 mg g <sup>-1</sup>	Inner-sphere La–O– Sb complex, ligand exchange, electro- static interaction, and H–bonding.	Wang et al. 2018
Horse manure	500°C,2h	Bi(NO <sub>3</sub> ) <sub>3</sub>	U(VI)	516.5 mg g <sup>-1</sup>	Surface complexa- tion, precipitation, ion exchange, and reductive reaction.	Liao et al. 2022
Bamboo shaving	480°C, 2 h	Mg/Al LDH	Cr(VI)	38 mg g <sup>-1</sup>	New layered double hydroxides interca- lated with $Cr_2O_7^{2-}$ , phsysical adsorption, surface adsorption, interlayer anion exchange, and precipitation.	Huang et al. 2019a
Peanut shell	250°C,2h	FeS and starch	U(VI)	76.32 mg g <sup>-1</sup>	Electrostatic attrac- tion, surface com- plexation, precipita- tion, and reductive reaction.	Liu et al. 2021a
Peanut shell	500 °C, 2 h	<i>Pseudomonas hibiscicola</i> strain L1 immobilization	Cr(VI) Cu(II) Ni(II)	38.2% 45.8% 81.2%	Complexation, ion exchange, precipita- tion, and reduction.	An et al. 2022

## Table 1 (continued)

For cationic heavy metals (e.g., Cd, Pb, Cu, Zn, and Ni), their adsorption by engineered biochar is greatly influenced by biochar's surface area, zeta potential, mineral components, and surface functional groups and solution conditions (Shaheen et al. 2019). For example, engineered biochar by ball milling was found to be an effective adsorbent for Cd(II), showing an excellent adsorption capacity  $(922 \text{ mgg}^{-1})$  (Ramanayaka et al. 2020). Ball milling resulted in the enhancement of functional groups on the biochar surface, i.e., -OH, C=O, and amine groups, which favored the adsorption via complexation between Cd ions and functional groups. Furthermore, cadmium exists as a cation in aqueous media and can be bonded by the negatively-charged biochar surface via electrostatic attraction (Ramanayaka et al. 2020). In another study, Yu et al. (2018) reported that N-doped corn straw-derived biochar owned a high graphitic-N percentage (46%) and improved surface area  $(419 \text{ m}^2 \text{g}^{-1})$ . Accordingly, the N-doped biochar showed an excellent adsorption capacity for Cd(II) (197.8 mg  $g^{-1}$ ). In addition to physical adsorption, the adsorption mechanisms were mainly governed by complexation with graphitic-N and hydroxyl groups and Cd(II) $-\pi$  bonding (Yin et al. 2020). In parallel, Deng et al. (2017) developed a chitosan/pyromellitic dianhydride (PMDA) modified biochar (CS/PMDA-BC) to remove Cd, Pb, and Cu in ternary solutions. It was noted that CS/PMDA-BC exhibited effective removal of these three cations, and the selective adsorption capacity for Cu(II) was also observed. The authors concluded that introduced N-containing groups after loading of chitosan and PMDA was the plausible reason for the adsorption enhancement. In addition, immobilization of microbes onto biochar has been reported to enhance the removal of Cu(II) and Ni(II) from aqueous solutions (An et al. 2022). The authors introduced Pseudomonas hibiscicola strain L1 onto peanut shell biochar, and the removal rate of bacteria-loaded biochar for Cu(II) and Ni(II) was 45.8% and 81.2%, respectively. The involved mechanisms were ascribed to complexation, ion exchange, precipitation, and enhanced bio-adsorption by strain L1.



Typically, Cr, As, and Sb exist as anions in aqueous media, and their negatively charged surface nature results in the electrostatic repulsion with negatively charged biochar surface. Therefore, the adsorption ability of pristine biochar to such elements is limited and modification is necessary to enhance their removal by biochar. For instance, Zhang et al. (2020b) found that loading of chitosan onto bamboo-derived biochar could facilitate Cr(VI) adsorption, with maximum adsorption capacity up to 127 mgg<sup>-1</sup>, which was due to the electrostatic attraction between  $-OH^+/-NH_2^+$  and  $CrO_4^{2-}$ . Liang et al. (2020) used KOH and N-doping to activate the biochar produced from glucose at 800°C. A significant adsorption capacity of modified biochar for Cr(VI) was achieved as  $402.9 \text{ mg g}^{-1}$ , and different mechanisms such as physisorption, electrostatic attraction, surface complexation, and reduction of Cr(VI) into Cr(III) and subsequent adsorption and precipitation of Cr(III) species were involved (Liang et al. 2020). In another study, iron-modified Populus L. derived biochar was prepared using FeCl<sub>3</sub> (Xu et al. 2020), and As(III) removal by Femodified biochars was up to 99.9%, which was mainly due to the formation of Fe-As complex as highlighted by X-ray fluorescence analysis. Simultaneously, the oxidation of labile As(III) to non-labile As(V) species was noted, which was ascribed to the change in solution pH (Xu et al. 2020). Rahman et al. (2021) fabricated a biosolid-derived biochar modified by zirconium (Zr) and Fe (Zr-Fe/BC) for As(V) removal. The maximum adsorption capacity of As(V) reached up to  $62.5 \text{ mg g}^{-1}$ , while that of the pristine biochar was only  $15.2 \text{ mgg}^{-1}$ . The presence of Zr and Fe could facilitate As(V) adsorption through the formation of complexes of Zr-O-As, Fe-O-As, and Zr-O-Fe-As. Electrostatic interaction and hydrogen bonding also participated in the removal of As(V). Similar to As, Sb is another typical metalloid in aqueous media. Metal oxides, sulfide and carbon nanomaterials have been employed to functionalize biochar for the removal of aqueous Sb (Jia et al. 2020; Chen et al. 2022b). For example, Wang et al. (2018) prepared lanthanum (La) doped magnetic biochar and its adsorption for Sb(V) was greatly improved, increased from 2.2 to  $18.9 \,\mathrm{mg g^{-1}}$ (pH7.0). FTIR and XPS analyses revealed that the dominant mechanism for enhanced Sb(V) adsorption was the formation of inner-sphere La-O-Sb complex.

In addition to these more popularly studied metal(loid) s above, there are also studies focusing on the removal of mercury (Hg) (O'Connor et al. 2018; Lyu et al. 2020b), uranium (U) (Liu et al. 2021a; Lyu et al. 2021), rare earth elements such as vanadium (V) (Ghanim et al. 2020) and

lanthanum (Lakshmi et al. 2021), etc. by engineered biochar reported recently, but it is still a relatively nascent area of research. The choice of modification method is very different for different target pollutants. To maximize both the environmental and economic benefits, appropriate functionalization methods should be applied to tailor the surface properties of biochar and thus to enhance the adsorption efficiency for target contaminants.

## 4.1.2 Nutrients

Phosphate, nitrate and ammonium are the typical forms of nutrients in water bodies that directly lead to eutrophication and ecosystem toxicity (Long et al. 2019). Engineered biochar has been used to enhance the removal of such inorganic pollutants in aqueous phase, as summarized in the Supplementary Materials (Table S2). Huang et al. (2020b) found that wheat straw biochar after introduction of chitosan enhanced the phosphate removal from aqueous solution with the maximum adsorption capacity of  $109 \text{ mgg}^{-1}$ . Electrostatic interaction, ligand exchange, and Lewis acid-base interaction were the main mechanisms during the phosphate removal by chitosan-loaded biochar (Huang et al. 2020b). Sornhiran et al. (2022) prepared a series of biochars modified using different metal salts (i.e., AlCl<sub>3</sub>, FeCl<sub>3</sub>, MnCl<sub>2</sub>, ZnCl<sub>2</sub>, MgCl<sub>2</sub>) to remove phosphate in the water bodies, FTIR and XPS results verified that precipitation between metal oxides and phosphate was the predominant mechanism. In parallel, biochars modified by various methods such as ball milling (Qin et al. 2020; Feng et al. 2022), acid-base activation (Hu et al. 2018; Wang et al. 2020c), and metal oxides modification (Long et al. 2019) have been reported to be excellent adsorbents in the removal of aqueous nitrate and/or ammonium. It is worth mentioning that recent studies have shown the potential of combining denitrifying bacteria and biochar to remove nitrate (Zhang et al. 2021b; Zheng et al. 2021; An et al. 2022). For instance, Pseudomonas hibiscicola strain L1 immobilization on the peanut shell biochar achieved 65.29% removal of nitrate (An et al. 2022). A general conclusion can be made that the modifications changed biochar surface chemistry, thereby enhancing nutrients adsorption. The removal mechanisms of nutrients by engineered biochar mainly involved electrostatic interaction, precipitation, surface complexation, ligand exchange, Lewis acid-base interaction and biological adsorption.

#### 4.1.3 Organic pollutants

Organic contaminants including dyes, pesticides, antibiotics, plasticizers, polycyclic aromatic hydrocarbons (PAHs), and phenols are major types of pollutants in the aquatic environment (Ahmed et al. 2016). Table 2 presents the removal of typical organic contaminants by engineered biochar, and the associated mechanisms are also summarized. Various mechanisms govern the adsorption of organic pollutants onto biochar, which mainly contain pore-filling, hydrophobicity, electrostatic interactions, hydrogen bonding, partition, and cation/ $\pi$ - $\pi$  interactions (Ni et al. 2011; Zhao et al. 2017; Luo et al. 2022). Biodegradation of organic pollutants by bacteria could also be a key mechanism, if the biochar is enriched with target microorganisms through biological modification process (Zhou et al. 2021a). The related removal/immobilization mechanisms of target organic pollutants by engineered biochar are depicted in Fig. 4.

For dyes, Yek et al. (2020) employed microwave and steam modifications to activate orange peel-derived biochar pyrolyzed at 950°C, and the activated biochar had enhanced adsorption capacity for Congo red  $(136 \text{ mgg}^{-1})$ . Moreover, a sulfur-doped biochar originated from tapioca peel waste was found to be a good adsorbent for malachite green  $(30.2 \text{ mgg}^{-1})$  and rhodamine B ( $33.1 \text{ mg g}^{-1}$ ), and electrostatic attraction, surface complexation and hydrogen bonding were considered as the key removal mechanisms (Vigneshwaran et al. 2021). Regarding pesticides, a magnetic sludge biochar modified by graphene oxide (GO/CoFe<sub>2</sub>O<sub>4</sub>-SBC) was synthesized and used to remove imidacloprid (Ma et al. 2021b). The maximum adsorption capacity for imidacloprid by  $GO/CoFe_2O_4$ -SBC was noted as 8.64 mgg<sup>-1</sup>, which was ascribed to enlarged surface area,  $\pi - \pi$  conjugation between graphitic structure/-OH and the pollutant, and more available binding sites (e. g. C-O, Fe-O, Co-O). In a different study, atrazine removal using iron-modified biochar loaded with Acinetobacter lwoffii DNS32 (bFeMBC) was explored by Tao et al. (2019). The maximum removal rate was 8.56 and 9.71 mg  $L^{-1}h^{-1}$ , for single bacteria and bFeMBC treatment, respectively. The enhanced removal might be attributed to two aspects: 1) iron oxide nanoparticles can catalyze free radical reactions to generate •OH and thus attack atrazine; 2) ironmodified biochar can promote bacterial growth and biodegradation of atrazine.

A considerable amount of literature has described the engineered biochar application in antibiotic removal. For instance, Zeng et al. (2022) used  $H_3PO_4$  to activate the coffee ground derived biochar for the removal of sulfadiazine. Governed by hydrophobic effect and  $\pi - \pi$  EDA interaction, the modified biochar showed a high sulfadiazine adsorption up to 139.2 mg g<sup>-1</sup>. In another study, glucose-derived biochar doped with N and Cu was efficient in catalyzing oxidative degradation of tetracycline in the persulfate activation (Zhong et al. 2020). The targeted biochar showed a large surface area of 352 m<sup>2</sup> g<sup>-1</sup>, and abundant functional groups (e.g., -OH), which resulted

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Table 2 Urganic	contaminant remova	il and associated mechanism	s by engineered biochars in	aqueous system		
Feedstock	Pyrolysis conditions	Modification method	Organic pollutants	Removal efficiency or capacity	Mechanisms involved	References
Bamboo	500°C, 2 h	Steam activation	Tetracycline	95.75%	Hydrogen bonding, electro- static interaction, and π-π electron donor-acceptor interactions.	Wang et al. 2020a
Orange peel waste	950°C, 20 min	Microwave and steam activa- tion	Congo red	136 mgg <sup>-1</sup>	Physical adsorption, electro- static interaction, and surface complexation with sulfonic groups.	Yek et al. 2020
Phragmites australis	280°C, —	Urea	Phenanthrene	1.97 mg g <sup>-1</sup>	л-т interactions, hydropho- bic effect, and electrostatic attraction.	Wang et al. 2020b
Cassava waste	500°C, 1 h	ЮН	Norfloxacin, Sulfamerazine Oxytetracycline	5.00 mg g <sup>-1</sup> 0.67 mg g <sup>-1</sup> 10.0 mg g <sup>-1</sup>	Electrostatic interactions, $\pi$ – $\pi$ interactions, and H-bonds.	Luo et al. 2018a
Chitosan	800°C, 2 h	KOH, urea	Chloramphenicol Florfenicol Thiamphenicol	786.1 mgg <sup>-1</sup> 751.5 mgg <sup>-1</sup> 691.9 mgg <sup>-1</sup>	Pore-filling, hydrophobic effect, hydrogen bonding, and π–π EDA interaction.	Liu et al. 2019
Cotton straw	900 °C, 2 h	K <sub>2</sub> CO <sub>3</sub> CaCO <sub>3</sub>	Diethyl phthalate (DEP)	657 mgg <sup>-1</sup>	Mostly dominated by pore filling; Lewis acid-base inter- action, <i>m</i> - <i>m</i> stacking interac- tion, hydrogen bonding, and partitioning.	Cheng et al. 2022
Hickory chip	600 °C, 2 h, vacuum atmosphere	Ball milling	Reactive red	34.8 mg g <sup>- 1</sup>	Increased O-moieties and N-containing functional groups favored the pollutant removal via electrostatic interaction.	Xu et al. 2021
Poplar woodchip	300°C, 3 h	Ball milling	Enrofloxacin	80.2%	Enhanced photocatalytic performance of ball milled biochar was due to the generated radicals $O_2^*$ and $h^+$ .	Xiao et al. 2020
Coffee ground	700°C, 1 h	$H_3PO_4$	Sulfadiazine	139.2 mg g <sup>-1</sup>	Hydrophobic effect and $\pi$ – $\pi$ EDA interaction.	Zeng et al. 2022
Pinewood	400°C, 0.5 h	H <sub>2</sub> O <sub>2</sub>	Methylene blue	7.71 mg g <sup>-1</sup>	$\pi$ - $\pi$ interaction between the dye and the biochar.	Huff and Lee 2016
Waterworks sludge	800°C, 1.5 h	Dicyandiamide, Fe(OH) <sub>3</sub> , and H <sub>2</sub> SiO <sub>3</sub>	Methylene blue	300.36 mg g <sup>-1</sup>	Electrostatic attraction, hydro- gen bonds, n-n interaction, and pore filling.	Xi et al. 2022
Biogas residue	700°C, 2h	Potassium ferrate	Benzola]pyrene	47.8%-87.0%	Radical pathway: SO <sub>4</sub> " and O <sub>2</sub> ". O <sub>2</sub> " Non-radical pathway: <sup>1</sup> O <sub>2</sub> and electron transfer	Li, Yu, Chen, et al., 2022

Table 2 (continu	ed)					
Feedstock	Pyrolysis conditions	Modification method	Organic pollutants	Removal efficiency or capacity	Mechanisms involved	References
Kenaf bar	600 °C, 2 h	nZVI assisted with persulfate system	2,4-dichlorophenol	91%	SO4" and •OH were primary radicals responsible for the degradation, and reductive dechlorination reaction by nZVI.	Diao et al. 2020
Tapioca peel waste	800°C, 3h	S doping	Malachite green Rhodamine B	30.18 mgg <sup>-1</sup> 33.10 mgg <sup>-1</sup>	Electrostatic attraction, sur- face interaction and hydrogen bondings.	Vigneshwaran et al. 2021
Peanut shell	350°C, 1 h	N and S doping	DEP	14.3 mg g <sup>-1</sup>	Enhanced removal by forma- tion of the pyridinic N and oxidized S groups on biochar.	Guo et al. 2020
Glucose	700°C, 3 h	N and Cu doping	Tetracycline	100%	Radical degradation involving •OH and electron transfer.	Zhong et al. 2020
Hickory wood chip	600°C, 1 h	MgO, ball milling	Methylene blue	87.5%	Physical adsorption, electro- static attractive force, and surface complexation.	Zheng et al. 2020
Corncob	600°C, 1 h	chitosan	Ketoprofen	120-131 mg g <sup>-1</sup>	Hydrogen bonding, $\pi$ – $\pi$ interaction, electrostatic interaction, and pore filling.	Chen et al. 2021b
Pine needle	500°C, 2h	MnCl <sub>2</sub> ·4H <sub>2</sub> O and FeCl <sub>3</sub> ·6H <sub>2</sub> O	Naphthalene	48.9% (under dark)	Catalytic performance of Fe(II), Mn(II), $O_2^{-}$ to generate •OH to oxide naphthalene.	Li et al. 2019
Wood biomass	700°C, 2h	Graphene oxide	Dimethyl phthalate (DMP)	45.65 mg g <sup>-1</sup>	$\pi$ - $\pi$ interactions and hydro- phobicity.	Abdul et al. 2017
Wood chip	600°C, 2h	Graphene oxide	DMP, DEP, dibutyl phthalate (DBP)	35.2 mg g <sup>-1</sup> 26.4 mg g <sup>-1</sup> 25.1 mg g <sup>-1</sup>	Pore diffusion, n-n interac- tions, and hydrophobic interaction.	Yu et al. 2020
Wheat straw	600°C, 1 h	Graphene	Phenanthrene	13.5 mg g <sup>-1</sup>	л-л interactions, partitioning and surface adsorption.	Tang et al. 2015
Sludge	500°C, 2h	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, FeCl <sub>3</sub> ·6H <sub>2</sub> O, graphene oxide	Imidacloprid	8.64 mg g <sup>- 1</sup>	Pore filling, n-n conjuga- tion, and functional groups interaction	Ma et al. 2021b
Bamboo	550°C, 1 h	Fe <sub>2</sub> O <sub>3</sub> , ZnO, CuO	Bisphenol A Sulfamethoxazole	263.2 mgg <sup>-1</sup> 212.8 mgg <sup>-1</sup>	H-bonding, hydrophobic, and π-π electron donor-acceptor interactions.	Heo et al. 2019
Sawdust	600°C, 2 h	Red mud	Perfluorooctane sulfonate	194.6mgg <sup>-1</sup>	Hydrophobic and elec- trostatic interaction, catalytic degradation, and ion exchange.	Hassan et al. 2020

Table 2 (continu	(pər					
Feedstock	Pyrolysis conditions	Modification method	Organic pollutants	Removal efficiency or capacity	Mechanisms involved	References
Bamboo	400°C, 1 h	Cu/Zn/Fe LDH	Atrazine	63.64–87.04 mg g <sup>-1</sup>	л-л interactions occurring at the interfaces, hydrogen bonding, and pore filling effects.	Lartey-Young and Ma 2022
Waste sludge	500°C, 2h	Mg/Fe LDH	Doxycycline	88.76%	Radical pathway: •OH, SO <sub>4</sub> <sup>-</sup> , and O <sub>2</sub> <sup></sup> Non-radical pathway: <sup>1</sup> O <sub>2</sub>	Ma et al. 2021a
Ginkgo biloba rods	500°C, 3 h	Phytic acid	Ponceau 2R	%66	Metaphosphoric acid cata- lyzed the production of •OH to degrade Ponceau 2R.	Hua et al. 2022
Corn stalk	600°C, 2 h	Fe(NO <sub>3</sub> ) <sub>3</sub> -9H <sub>2</sub> O and loaded with <i>Acinetobacter lwoffii</i> DNS32	Atrazine	9.71 mg L <sup>-1</sup> h <sup>-1</sup>	Biodegradation by DNS32 strain, H-bonding, hydroxyl radicals reaction, and biochar adsorption (mainly n-n interaction).	Tao et al. 2019
Erding	500°C, 1h	<i>Bacillus cereus</i> LZ01 immobi- lization	Chlortetracycline	82.3%	Biodegradation by LZ01 and biochar adsorption.	Zhang and Wang 2021
Corn straw	I	Vibrio sp. LQ2 immobilization	Diesel oil	94.7%	Biodegradation and minor physical adsorption.	Zhou et al. 2021a



in almost 100% removal for tetracycline. Quenching experiments and EPR analysis revealed that the main degradation reaction was •OH-induced degradation via free radical pathway, and the biochar-mediated electron transfer between tetracycline and persulfate via non-radical pathway. Additionally, biochar loaded with *Bacillus cereus* LZ01 also showed a removal rate of 82.3% for chlortetracycline via biodegradation by LZ01 and biochar adsorption (Zhang and Wang 2021).

Engineered biochar has also been used to remove the aqueous phthalate esters (PAEs) (Guo et al. 2020). A graphene oxide modified biochar was prepared, and its adsorption capacity for different PAEs was investigated, i.e.,  $35.2 \text{ mgg}^{-1}$  for dimethyl phthalate (DMP),  $26.4 \text{ mgg}^{-1}$  for diethyl phthalate (DEP), and  $25.1 \text{ mgg}^{-1}$ for dibutyl phthalate (DBP) (Yu et al. 2020). Interestingly, the authors concluded that the dominant mechanism differed for different PAEs, namely pore filling for DMP,  $\pi$ – $\pi$ interaction for DEP, and hydrophobic effect for DBP. Guo et al. (2020) reported that the DEP adsorption capacity of N and S co-doped peanut shell biochar was higher than that of raw biochar (14.34 mg g<sup>-1</sup> vs 6.57 mg g<sup>-1</sup>). Recently, Cheng et al. (2022) produced a series of hierarchical porous biochars (HPBs) using K<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub> as the activators, with a maximum specific surface area of up to 2554 m<sup>2</sup> g<sup>-1</sup>. The maximum adsorption capacity for DEP by the resultant HPB<sub>KCa-1</sub> (biochar produced at the mol ratio of K to Ca was 1: 1) reached 657 mg g<sup>-1</sup>. Owing to the remarkably enlarged pore structure, it is deemed that the DEP adsorption was mostly dominated by pore filling; however, other mechanisms such as Lewis acid-base interaction, hydrogen bonding, and partitioning might also involve.

In relation to PAHs, Fe-impregnated biochar coupled with ammonium persulfate (FBC-APS) showed superior performance for degradation of benzo[a]pyrene (BaP) (Li et al. 2022b). The degradation rate of BaP increased from 47.8% to 87.0% as the doses of FBC increased from  $0.125 \text{ gL}^{-1}$  to  $0.5 \text{ gL}^{-1}$ . Two pathways were involved in the degradation of BaP: 1) radical pathway mediated by

 $SO_4^{\bullet-}$  and  $O_2^{\bullet-}$ ; 2) non-radical pathway via  ${}^1O_2$  contribution and electron transfer. Moreover, Wang et al. (2020b) developed an N-doped *Phragmites australis*-derived biochar. Its adsorption capacity for phenanthrene was reported as  $1.97 \text{ mg g}^{-1}$ . Characterization analysis and DFT calculations indicated that the phenanthrene removal was majorly dominated by  $\pi-\pi$  interactions, hydrophobic effect, and electrostatic attraction.

Phenolic compounds including phenol, bisphenol A (BPA), pentachlorophenol (PCP) and p-nitrophenol (PNP) are typical organic contaminants in aquatic environment (Huang et al. 2019b). Removal of phenolic substances is also one of the research directions of engineered biochar's environmental applications. For example, Heo et al. (2019) synthesized CuZnFe<sub>2</sub>O<sub>4</sub>-biochar composite (CZF-BC) by a facile one-pot hydrothermal method. CZF-BC exhibited great adsorption performance in the removal of BPA ( $263.2 \text{ mg g}^{-1}$ ), which could be attributed to H-bonding, hydrophobic effect, and  $\pi$ - $\pi$  interaction. In addition, the potential of engineered biochar has also been investigated for the removal of perfluorinated compounds (Hassan et al. 2020) and pharmaceuticals (Shan et al. 2016; Fu et al. 2020) from water bodies.

## 4.2 Soil systems

#### 4.2.1 Metal(loid)s

Due to the vast anthropogenic activities, agricultural soils are polluted with a diverse range of metal(loid)s and organic pollutants (Chen et al. 2021a). Engineered biochar is accepted as a cost-effective soil-remediation material to alleviate the environmental stress of contaminated soils. The remediation mechanisms include the direct process (i.e., immobilization/degradation of contaminants by biochar) and indirect process (i.e., improved soil properties by biochar) in the complex terrestrial system (Chen et al. 2022a). The multiple engineered biochars and their remediation performances for metal(loid)s in soils are summarized in the Supplementary Materials (Table S3).

In a pot experiment, Zubair et al. (2021) amended a Cd-spiked soil ( $20 \text{ mg kg}^{-1}$ ) with 5% textile waste biochar (TWB), chitosan (CH), combined application of TWB and CH (w: w=1: 1) and CH-coated TWB (CH-BC), respectively. They found that the CH-BC treatment showed the greatest efficiency in decreasing Cd concentrations in soil (58%), and Cd uptake in plant shoot (73%) and root (54%), relative to the control. CH-BC offered negative sites to efficiently bind Cd<sup>2+</sup> ions via surface complexation, precipitation and cation exchange. The increased soil pH also strongly influenced the mobility and phytoavailability of Cd. High soil pH may increase the negative charge of the soil, which may favor Cd immobilization via electrostatic attraction. Furthermore, increased soil pH facilitated the formation of hydroxyl bound species of Cd (i.e., CdOH<sup>+</sup>). In a different study, Irshad et al. (2022) reported that 2% goethite-modified biochar amendment could reduce As uptake in rice grains by 77%, relative to the control. The goethite-modified biochar increased the Fe oxide content in soils, which promoted the formation of root Fe-plaque, and ultimately decreased As content in rice grains. Studies have also been conducted using other types of biochar involving different engineering methods such as sulfur power (O'Connor et al. 2018), Mg-Al LDH (Lyu et al. 2021), ultraviolet activation (Zhang et al. 2021c), cetyltrimethylammonium bromide (CTAB) loading (Murad et al. 2022), polyethyleneimine (PEI) modification (Tang et al. 2022), etc. to remediate metal(loid) contaminated soils.

However, agricultural soils are often simultaneously contaminated with multiple metal(loid)s. Therefore, many researchers have also reported that effect of engineered biochars in the immobilization of various metal(loid)s in co-contaminated soils. Wang et al. (2019b) prepared MnFe<sub>2</sub>O<sub>4</sub>-modified biochar derived from tea branches, and explored the effect of its application with different dosages (0.1%, 1% and 2%) on the remediation of Sb and Cd from the contaminated soil. The result of this study demonstrated that MnFe<sub>2</sub>O<sub>4</sub>-modified biochar amendment at 2% dose simultaneously decreased the concentration of bioavailable Sb and Cd in soil by 43.5% and 76.0%, respectively. However, the pristine biochar only reduced the bioavailable Cd concentration in soil (12.7%–33.9%). In another study, Liu et al. (2018) evaluated the influence of coconut shell biochar (CSB) and modified biochar after ultrasonication and HCl activation (MCSB) on the availability of Cd, Ni, and Zn in multi-metal contaminated soils. After 63 d of incubation, application of MCSB at 5% dose decreased the concentration of bioavailable Cd, Ni and Zn by 30.1%, 57.2% and 12.7%, respectively, compared to the control. The MCSB contained sufficient active functional groups (e.g., -OH, -COOH, C=O), and its application increased soil pH and CEC, which subsequently decreased the mobility of metal ions in the soil via electrostatic attraction, surface complexation, and cation exchange.

## 4.2.2 Organic pollutants

In addition to immobilization of metal(loid)s, biochars functionalized by steam/ $CO_2$  activation, ball milling, oxidizing, iron materials, LDH, organic surfactants, and bacteria loading for the remediation of various organic pollutants (e.g., pesticides, antibiotics, plasticizer, PAHs, and phenols) in soil have been reported and are

summarized in the Supplementary Materials (Table S4). Specifically, a sulfidated nano zerovalent iron (S-nZVI) loaded biochar (S-nZVI@BC) at an S-nZVI: biochar mass ratio of 3:1 was successfully synthesized by Gao et al. (2022). Resultant biochar at 1% dosage showed superior degradation for nitrobenzene with a removal rate of 98% within 24 h. The authors confirmed that the solubilization effect by biochar and reduction by FeS, were the dominant mechanisms for nitrobenzene removal. In addition, S-nZVI@BC also had excellent antioxidant capacity and kept a high removal efficiency for nitrobenzene (73%) after aging for 14 weeks, which suggested that this special biochar had the potential for the field application (Gao et al. 2022). In another study, olive tree pruning residues were first pyrolyzed at 400 °C for 2 h, and 0.025 M KMnO4 was used as an oxidizing agent to obtain the modified biochar with high redox capacity for the remediation of pentachlorophenol (PCP) (Chacón et al. 2022). KMnO<sub>4</sub>-modified biochar exhibited the highest maximum rate of remediation ( $k_{max}$ ) under aerobic (3.73  $\mu g_{PCP}$  $g_{soil}^{-1} d^{-1})$  and anaerobic (2.40  $\mu g_{PCP} g_{soil}^{-1} d^{-1})$  conditions, which was much higher than that of raw biochar. Moreover, Bacillus-siamensis-inoculated biochar was synthesized to minimize dibutyl phthalate (DBP) pollution in agricultural soils (Feng et al. 2020). The bacterialoaded biochar could enhance the DBP biodegradation by simultaneously raising the degradation rate constant from 0.20 d<sup>-1</sup> to 0.24 d<sup>-1</sup>, and half-life from 2.31 d to 2.11 d. A significant reduction of DBP uptake by leafy vegetables was also observed, which could be attributed to the enhanced adsorption/degradation by biochar and Bacillus siamensis strain T7.

#### **5** Conclusions and future perspectives

In this article, we thoroughly discussed the functionalization of biochars using various modification methods and characterizations of engineered biochars. Furthermore, we highlighted the utilization of engineered biochar for the decontamination of aquatic and soil systems polluted by (in)organic contaminants. The specific properties of engineered biochar such as improved surface area, introduction of new functional groups, and enhanced electron transport capacity are the key factors affecting the decontamination efficiency in multifunctional applications, as revealed by the literature reviewed. In general, engineered biochar is an environmentally friendly adsorbent/ catalyst/amendment that can be used to address multiple environmental concerns. However, some issues remain unresolved and the following need to be considered to achieve a sustainable future for engineered biochar in environmental applications.

- Physical and chemical modification methods have often been used to synthesize engineered biochar. The synthesis of engineered biochar using biological modification methods involving microorganisms needs to be explored in detail in relation to its value in the remediation of organic contaminants in aquatic and soil systems.
- To date, the published results using engineered biochar are majorly based on laboratory tests. The long-term field-scale experiments using engineered biochar are required to be conducted to evaluate its practical applications.
- Engineered biochar undergoes long-term weathering by abiotic and biotic aging when exposed to environmental conditions. However, little is known about the remediation efficiency of aged engineered biochar. Further research is needed to explore the stability of its remediation potential with aging process and mechanisms affected by different functionalization methods.
- One of the important benefits of modification is to achieve easy removal of spent biochar after water treatment, e.g., magnetization, and the practical feasibility for recycling magnetic biochar needs to be investigated at pilot scale. In addition, there is insufficient information on the safe disposal of spent engineered biochar after adsorption of toxic pollutants. Therefore, related technology should be developed to recover the spent engineered biochar, such as utilization of specific eluents to efficiently desorb the target contaminant. Moreover, non-renewable spent engineered biochar should also be used for energy production or nutrient source (in the case of N and P laden biochar after adsorption) from economic and environmental perspectives.
- The presence of heavy metals, PAHs, and persistent free radicals (PFRs) on the biochar has been reported. Moreover, some modification processes may introduce new hazardous chemicals. The ecotoxicity and stability of such potentially hazardous biochars should be evaluated from an ecotoxicological point of view, such as the release of toxic chemicals over long-term.
- The quality and remediation performance of engineered biochar can be affected by the type of original feedstock, pyrolysis conditions and modification methods. A combined approach following the experimental and modelling results should be implemented to establish standards for biochar production, characterization and life cycle assessment processes.
- Advanced spectroscopic analysis methods such as synchrotron-based X-ray absorption fine structure

(XAFS) spectroscopy and computational approaches based on density functional theory (DFT) and molecular dynamics (MD) calculations should be considered to reveal the decontamination mechanisms for various pollutants. Artificial intelligence and machine learning should be employed as effective techniques to optimize the development of engineered biochar, and further automate and forecast the remediation process.

 In the context of carbon neutrality worldwide, biochar as a carbon-negative technology has received a wide attention. However, quantitative estimation methods of carbon sequestration by engineered biochar are missing, and the potential carbon sequestration value of engineered biochar has not been effectively verified and developed.

## Supplementary Information

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Additional file 1: Text S1. Characterization techniques for engineered biochar. Table S1. Contaminants removal and associated mechanisms by nonmetallic heteroatom doped biochar. Table S2. Nutrient removal and associated mechanisms by engineered biochars in aqueous system. Table S3. Summary of multiple engineered biochars and their immobilization performance for metal(loid)s in soils. Table S4. Summary of multiple engineered biochars and their or organic pollutants in soils.

#### Authors' contributions

Hanbo Chen: conceptualization, literature search, collection and analysis, writing—original draft, review and editing. Yurong Gao: writing—review and editing. Jianhong Li: writing—review and editing. Zheng Fang: writing—review and editing. Nanthi Bolan: formal analysis, writing—review and editing. Amit Bhatnagar: writing—review and editing. Bin Gao: writing—review and editing. Deyi Hou: writing—review and editing. Shengsen Wang: writing—review and editing. Hocheol Song: writing—review and editing. Xing Yang: writing—review and editing. Sabry M. Shaheen: writing—review and editing. Jun Meng: writing—review and editing. Wenfu Chen: writing—review and editing. Jörg Rinklebe: writing—review and editing. Hailong Wang: conceptualization, supervision, writing—review and editing. The authors read and approved the final manuscript.

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#### Availability of data and materials

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

## Declarations

#### **Competing interests**

The authors have no conflicts of interest to disclose, financial or otherwise.

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