

**Application of biochars in the remediation of chromium contamination:
Fabrication, mechanisms, and interfering species**

Zheng Chujing, Yang Zhihui, Si Mengying, Zhu Feng, Yang Weichun, Zhao Feiping, Shi Yan

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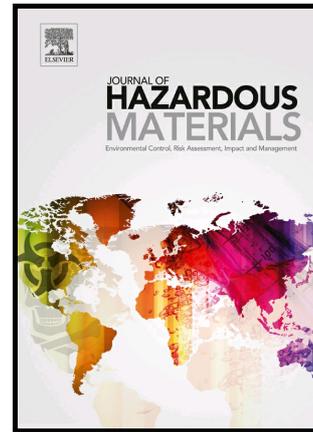
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Application of biochars in the remediation of chromium contamination: Fabrication, mechanisms, and interfering species

Chujing Zheng^a, Zhihui Yang^{a,b}, Mengying Si^a, Feng Zhu^{a,b}, Weichun Yang^{a,b}, Feiping Zhao^{a,b}, Yan Shi^{*a,b}

^a School of Metallurgy and Environment, Central South University, Changsha 410083, China

^b Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Changsha 410083, China

Abstract

Chromium (Cr) is one of the most toxic pollutants that has accumulated in terrestrial and aqueous systems, posing serious risks towards living beings on a worldwide scale. The immobilization, removal, and detoxification of active Cr from natural environment can be accomplished using multiple advanced materials. Biochar, a carbonaceous pyrolytic product made from biomass waste, is considered as a promising material for the elimination of Cr contamination. The preparation and properties of biochar as well as its remediation process for Cr ions have been well investigated. However, the distinct correlation of the manufacturing, characteristics, and mechanisms involved in the remediation of Cr contamination by various designed biochars is not summarized. Herein, this review provides information about the production, modification, and characteristics of biochars along with their corresponding effects on Cr stabilization. Biochar could be modified via physical, hybrid, chemical, and biological methods. The remediating mechanisms of Cr contamination using biochars involve adsorption, reduction, electron shuttle, and photocatalysis. Moreover, the coexisting ions and organic pollutants change the pattern of the remediating process of

* Corresponding author at: Institute of Environmental Science and Engineering, School of Metallurgy and Environment, Central South University, Changsha 410083, Hunan, China. E-mail: shiyzyrs@csu.edu.cn (Y. Shi); Fax: +86-0731-88710171; Tel: +86-0731-88830875

biochar in actual Cr contaminated water and soil. Finally, the present limitations and future perspectives are proposed.

Keywords Chromium; Biochar; Redox-active moieties; Pyrolysis; Electron shuttle; Photocatalyst

1 Introduction

Heavy metals released from anthropogenic activities, such as metal mining, smelting, and processing, have been considered as fatal threats to humans [1-6]. Among heavy metals, chromium (Cr) has aroused great public concerns because of its widespread distribution and redox sensitivity [7, 8]. It is one of the most common heavy metal species in the wastewater by-products of industries (*e.g.*, pigment and electroplating), and it is listed as one of the top-priority pollutants by the United States Environmental Protection Agency [9]. The World Health Organization has stipulated 50 µg/L as the maximum contaminant levels for CrO_4^{2-} in drinking water [10].

Chromium occurs in different forms throughout the natural environment. It has been widely accepted that Cr mainly presents in the oxidation states of trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) in natural water and soil [11]. Cr(III) tends to exhibit itself as a cation, whereas Cr (VI) often exists as oxyanion species, such as chromate(CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and hydrogen chromate (HCrO_4^-) [12]. The mobility, toxicity, and bioavailability of Cr vary with its speciation. For example, Cr(III) has much lower toxicity and mobility than Cr(VI) [11]. Cr(III) often precipitates at natural pH values in the form of $\text{Cr}(\text{OH})_3$ or $\text{Fe}_x\text{Cr}_{(1-x)}\text{OH}_3$ [13]. Organomineral complex is another stable occurrence for Cr(III) species [14]. Therefore, the reduction of toxic Cr(VI) into stable Cr(III) is expected as an efficient way to recover chromate pollution in the soil and water systems. Currently, multiple technologies from the physical, chemical, and biological perspectives have been established for the remediation of Cr contamination [15-17] (**Table 1**). However, most of them involve energy consumption, high-cost instruments, low efficiency, complicated

implementation, or secondary pollution. Therefore, it is critical to develop more convenient, economic, and environmental harmonious strategies for the decontamination of Cr.

Table 1 Technologies for Cr remediation and their advantages and disadvantages

	Remediation technologies	Advantages	Disadvantages	References
physical	electrokinetics/ion exchange/membrane separation	in-situ, rapid, and simple	high economical and energetical cost	[18]
chemical	coagulation/adsorption/reduction/solvent extraction/soil washing	high-efficient	nutrient loss and decaying soil structure	[16]
biological	(bio)sorption/reduction/accumulation/mineralization/stabilization	environmentally friendly and non-destructive	long remediation period	[19]

Biochar is an emerging material that is manufactured by the decomposition of carbon-rich biomass under oxygen-limited pyrolysis [20, 21]. Generally, biochar is characterized by high alkalinity, large surface area (SA), exceedingly porous structure, abundant functional groups, and relative stability [6, 22, 23]. Remarkable progress has been made in the understanding of biochar as an environmental friendly and low-cost material for carbon sequestration, energy recovery, contamination relief, and nutrient supplementation [24, 25]. In recent decades, biochar has gained significant attention in the remediation of heavy metal contamination in terrestrial and aquatic environments. Hierarchical porosity and abundant functional groups of biochar provide appreciable adsorption sites for heavy metals, *e.g.*, Zn^{2+} , Cd^{2+} , Pb^{2+} , and $Cr_2O_7^{2-}$ [26-28]. Moreover, it has been proved that biochars are capable of transforming heavy metal ions into less toxic species, such as oxidizing As(III) into As(V) [29], and reducing Cr(VI) into Cr(III) [30, 31].

Several reviews have summarized the application of biochar on the remediation of heavy metals, especially with regard to cations, *e.g.*, Cd^{2+} , Hg^{2+} , Pb^{2+} , and Cu^{2+} [22, 32, 33]. Unlike these cationic heavy metals, Cr is redox-active and usually manifests in the anionic form, which implies its distinct environmental behavior and unique reaction with biochar. For example, the supplementation of biochar was a viable way to decrease the bioavailability of Cu, Pb, Ni, Zn, and Cd, but it had a negligible effect on Cr in sediments [34]. It has been recognized that the increase of pH resulted in the promotion of the remediation rates of biochar on As and Pb through oxidation and precipitation, respectively, however, the removal of Cr was suppressed by electrostatic repulsion and inhibited reduction [31, 35]. The disparate

mechanisms are proposed in the sorption of biochar on As (complexation and electrostatic interaction), Cr (electrostatic interaction, reduction, and complexation), Cd and Pb (complexation, cation exchange, and precipitation), and Hg (complexation and reduction) [33]. Currently, biochar has been extensively utilized for Cr remediation [36-38] due to its possible potential on both adsorption and valence transformation. However, the influence of the production, characteristics, and remediation mechanism towards Cr ion of designed biochar remain unclear, which inhibits the utilization of biochar in the removal of Cr. Therefore, the overarching objective of this study is to provide a comprehensive review of recent researches on biochar in relation to its various aspects, *i.e.*, modification, property, removal performance of Cr, and relevant mechanisms. The specific aims of this study are the following: 1) comparing modification methods and resulted remediation efficiency of biochar for Cr contamination; 2) summarizing the underlying mechanism involved in the remediation of Cr contamination by biochar; 3) introducing the response of biochar to the interfering species in contaminated water and soil; and 4) future research directions of biochar on the remediation of Cr contamination.

2 Production and characteristics of biochar

2.1 Preparation of pristine biochar

The application of biochar on the remediation of Cr contamination relies on its physicochemical characteristics, such as porosity, acidity, functionality, and stability [39-41]. Understanding how pyrolysis governs the characteristics of biochar is the key to predicting the final product property and, consequently, the remediation capacity for Cr contamination. Feedstock, thermal temperature, duration, heating rate, and atmosphere are the dominant variables of biomass pyrolysis. Feedstock and thermal temperature are the most essential factors in determining the properties of biochar [42, 43]. Therefore, we principally discuss the effects of these two factors on the properties of biochar.

2.1.1 Temperature

Surface, bulk, and molecular structure properties of biochar, which are affected by the heat treatment temperature (HTT), exhibit different impacts on Cr removal.

Surface functional groups of biochar influence Cr immobilization by offering adsorption sites and changing pH [22]. With the increase of HTT, the hydroxyls were oxidized to carboxyls, accompanied by the breakage of the H-bonding network [44, 45]. Aliphatic alcohol and other acid surface functional groups were transformed to neutral or basic fused aromatic groups [46]. Meanwhile, alkaline minerals contained in ash were accumulated in biochar when HTT increased [47]. Thus, biochars obtained at high HTT displayed high alkalinity as well as aromaticity [48]. Lower value of cation exchange capacity (CEC) was also achieved at high HTT due to the loss of O containing functional groups [48].

Molecular structure determined the environmental behaviors of biochar [49]. The structure phase transition of biochar involved three primary reactions of char formation (or dehydrogenation), depolymerization, and fragmentation [50]. The phase transition commonly occurred within the range of 400 to 500 °C [23] and was generally completed under 700 °C, except that the aromatic condensation usually happened at 1000 °C [49]. High HTT (>400°C) facilitated the formation of well-organized carbon layers (*e.g.*, graphitized structures), which dramatically increased the SA and pore volume [49], providing electrostatic adsorption sites for Cr ions [51]. However, this positive correlation is unexpected in some studies. The decreasing tendency of SA was found when HTT was higher than 700 °C [52], owing to the coalescence and blocking of pores by carbon softening, melting, fusing, and carbonization [53]. The generation of fused rings in the aromatic cluster was also improved under high HTT [54], which was favorable for the stability of biochar in Cr immobilization. The heating temperature not only had an impact on the structure of biochar but also changed the composition within the biochar leachate. For example, low HTT contributed to the production of humic-like and low molecular mass substance in dissolved biochar [55], leading to the excellent Cr reducing performance of low-HTT biochars [56]. The oxidized organic S tended

to accumulate in dissolved biochar under high HTT (>500 °C) [57], which may provide potential adsorption sites due to its optimal affinity to Cr [58].

2.1.2 Feedstock

Considering the accessibility and cost, agricultural and forestry residual (*e.g.*, straw, grass, wood chip, and sawdust), industrial waste (*e.g.*, industrial by-product and sewage sludge), and animal manure are common feedstocks used to prepare biochar for Cr immobilization [59-63]. The variation of feedstocks leads to the difference in component, structure, and chemical activity of biochar.

The general physicochemical characteristics of biochar, such as CEC, pH, and SA, are essential indexes that contribute to ion exchange, electrostatic interaction, and physical sorption with Cr ions, respectively [33, 49]. Biochar produced from plant biomass typically had a high CEC value [64]. In particular, nonwoody plant-derived biochar exhibited higher CEC values than the woody one, because of the higher percentage of O-containing functional groups in nonwoody biochar [64]. Conventionally, the value of CEC was negatively correlated with HTT; however, the CEC of sewage sludge-derived biochar was reported to increase with HTT increasing from 600 to 900 °C [65]. Generally, wood-derived biochar had lower pH and higher SA than biochar derived from straw, green waste, and algae [48].

The variation among the characteristics of biochars is mainly attributed to the different pyrolysis mechanisms of feedstocks. The biomacromolecules in feedstocks are mainly composed of hemicellulose, cellulose, and lignin. The cleavage temperatures for hemicellulose, cellulose, and lignin were in the ranges of 220 to 315 °C, 315 to 400 °C, and 160 to 900 °C, respectively [54]. Lignin is the most stable biomass component. The carbohydrates were totally lost at 350 °C, while the characterization of lignocellulosic moieties was not found at 400 °C [25]. Due to the different percentage of biomacromolecules, the mineralization rate of biochar decreased from the grass to the hardwood precursor [66].

Moreover, the role of metals in precursors has received increasing attention. The carbon content increased in lignocellulose-based biochar, but decreased in sludge-based biochar with

increasing HTT [67], owing to the fact that the rate of mineral enrichment was higher than that of carbonization [68]. Accordingly, lignocellulose-derived biochars exhibited high carbon retention and resistance to chemical and thermal oxidation [69]. With regard to the retention of contaminants, the mineral maintained in municipal waste was responsible for a greater degree of SA than that of plant-derived biochar [70], which resulted in more efficient Cr(VI) adsorption [60]. Some pilot experiments have been done to convert metal pollutants into mineral sources for biochar preparation. Red mud, a solid waste from steel industry, was utilized as a resource of mineral in biochar pyrolysis [71], and the steel pickling waste liquor was used as an iron pool [40]. The resultant metallic iron in biochar was clarified to enhance the adsorption and reduction of Cr(VI) [72]. Zinc contaminated corn stover was converted into nano ZnO and ZnS modified biochar by direct pyrolysis, which promoted the Cr(VI) adsorption [38]. Similarly, nano Mg(OH)₂ and MgO embedded biochar was formed via one-step pyrolysis of magnesium polluted leaves [73], producing possible adsorption sites for Cr species.

2.2 Modification

Generally, pristine biochars without pre- or post-modifications have lower sorption sites, functionality, and removal performance than those with modifications [36, 63, 74]. The removal efficiency may also be constrained by the oxyanion nature of Cr and the negative surface of biochar [75]. In addition, pristine biochars are difficult to be separated from environment matrix, reducing the feasibility of recycling [36, 76]. Currently, modification, which is classified into four categories (*i.e.*, physical, hybrid, chemical, and biological), has been conventionally adopted to overcome these shortcomings (**Fig. 1**).

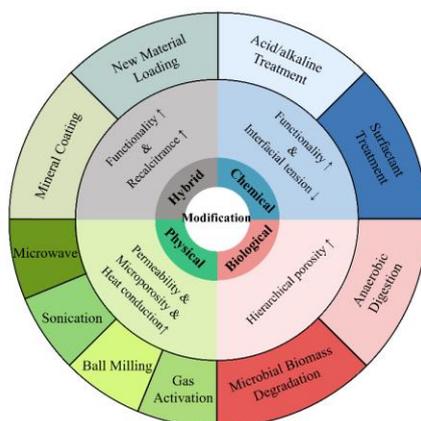


Fig. 1. Schematic diagram of biochar modification and its enhanced performance.

2.2.1 Physical modification

Physical modification consists of ball milling, microwave, sonication, *etc.* Generally, the precursor is pulverized into fine particles by mechanical force and activated by an energy field, offering plenty of adsorption sites to Cr [77-80].

Ball milling was utilized to improve the Cr immobilization capacities of biochar by reducing particle size, enlarging SA, and increasing functionality [81]. The resultant fine and even biochar particles were beneficial for heat conduction and mass transmission [82]. Additionally, the grinding process increased external and internal SA, pore volumes, and adsorption sites of biochar [83]. The physically modified biochar could turn into the nano-sized material after milling, exhibiting superior Cr(VI) adsorption capacity [83]. And because of the cleavage of aliphatic C–C and C–O bonds by mechanical force, the contents of functional groups, especially oxygen-containing functional groups, were increased, which facilitated the Cr removal by biochar [77].

Microwave was able to broaden the porous structure and drastically increase the SA of biochar in a short time, which contributed to the high capacity for Cr adsorption [84]. The activation using a microwave facilitated the conversion of acids, alcohols, phenols, ethers, alkyl halides, and ester groups, favoring carbonization during the charring period [85]. In order to obtain the same yield of biochar, microwave treatment needed less duration time and

temperature than conventional pyrolysis [78]. Therefore, microwave treatment was considered as a potential strategy for activation and alternative approach for pyrolysis [86], owing to its uniform heating process and high time-efficiency.

Gas activation (*e.g.*, CO₂, N₂, and H₂O activation) was a common method to promote the fabrication of biochar. It increased the rate of devolatilization, washed the trapped matter, broken the linkage of biomass, and converted lignocellulose into cellulose and lignin, thereby forming crystalline structures of biochar [82, 87]. Different gas components had distinct effects on the calcination process and properties of biochar. The pyrolytic decomposition of amorphous substances in CO₂ was faster than that in N₂ [88]. Moreover, the biochar produced under CO₂ was more porous, recalcitrant, hydrophilic, polar, and acidic than that produced under N₂ [88]. Considering the preferential range of pH for Cr(VI) immobilization, applying CO₂ medium could be an optimal approach to regulate the acidity of biochar. Similarly, H₂O activation, which is also called steam activation, promoted the degradation of hemicellulose in the process of carbonization [89]. With the presence of high content of O-containing functional groups and pore volume, steam activated biochar possessed higher SA than its counterpart under CO₂ activation [90]. This ideal SA in biochar was observed to significantly improve the adsorption for Cr(VI) [91, 92].

During the sonication, structure of biochar was optimized via nucleation, bubble growth, and bubble collapse. The microjets ensuing from ultrasonic assistance broke the graphic layer and leached them out, thereby cavitating the microspores within biochar [93]. After ultrasound treatment, the increasing microporosity and permeability of biochar provided the potential channels for subsequent Cr retention and chemical introduction [80].

2.2.2 Hybrid modification

Metal compound containing iron (Fe) [37, 81], zinc (Zn) [36, 94], magnesium (Mn) [75, 95], manganese (Mg) [96, 97], or aluminum (Al) [98] is one of the most well-studied hybrid materials applied in biochar modification. These hybrid metal compounds generally promoted Cr removal using biochar via the enhancement of chemisorption [75, 96, 99]. The level of SA,

porosity, and functionality determined the Cr adsorption capacity of hybrid-modified biochar. For example, the loading with MgO improved the porosity of biochar, mainly resulted from the volatile matters that were released from the reaction of MgCl₂ during pyrolysis [95]. Moreover, the incorporation of ZnO [36] and MnO resulted in the increasing SA and porosity of biochar because of the ideal functionality of hybrid materials [100]. In contrast, the coating of iron containing material enhanced the sorption ability of biochar but reduced the SA, due to the blockage of biochar pores [101]. The loading of iron oxides increased the zeta potential of biochar, thereby facilitating the electrostatic interaction between biochar and Cr anionic species [37]. The hydrolysis of Fe²⁺/Fe³⁺ in the preparation of iron-modified biochar decreased the pH of solutions, enhancing the potential Cr adsorption of biochar [37]. Besides adsorption, the hybrid of reductive metals such as nZVI [102], nano ZnO [36], and MnS [96] could facilitate Cr removal by enhancing the reduction of Cr(VI). In addition, the stability of modified biochar was an important parameter affecting the remediation of Cr contamination in the long-term. The dosing of iron and manganese containing materials reduced the stability of biochar through the formation of fragile Fe containing mineral [103] and unstable MnO during pyrolysis [104], respectively. However, high stability was achieved in an iron-modified biochar because of the generation of thermally inactive hematite [105]. Therefore, the stability of biochar was determined by the final phase of hybrid metal materials. The morphology pattern of hybrid containing metals versus HTT could be used to predict the stability of modified biochar. The iron structure was transformed from iron oxide, magnetite, iron protoxide, and iron carbide to elemental iron at temperature of below 400 °C, 400 to 500 °C, 650 °C, 800 °C, and 900 to 1000 °C, respectively [42]. Zero-valent iron was formed when HTT exceeded 700 °C [71]. The balance between adsorption capacity and recalcitrance should be considered when metal oxide is selected as the hybrid material.

Unlike metal oxide impregnation, the hybrid of clay mineral, such as montmorillonite, kaolinite, and calcite, facilitated the stability of biochar by increasing the condensed aromatic C proportion [106]. Concurrently, the addition of clay not only increased the concentration of aromatic, acidic, and phenolic carbon species, but also improved the pore volume of biochar, thereby providing potential adsorption sites for Cr ions [107]. Chitosan is an accessible

natural polysaccharide used to stabilize mineral, providing sorptive sites for Cr ions by numerous amine and hydroxyl functional groups [108]. The addition of chitosan was capable of restricting nano-particle agglomeration and promoting gluing of nano mineral onto biochar surface, which contributed to the optimal immobilization of Cr [109]. Other functional nanoparticles (such as carbon nanotubes, graphene oxide, and layered double hydroxides) have been reported to solder on biochar, resulting in desirable adsorption capacity [110]. In addition, graphene impregnation was able to strengthen the thermal stability of biochar, benefiting the resistance towards aging process [111].

2.2.3 Chemical modification

In the chemical modification, functional groups were endowed onto the surface of biochar through chemical reactions such as oxidation, nitration, amination, and sulfuration, providing active adsorption sites to Cr ions [58, 63, 75, 95]. Acid/alkali modification is a typical method for the recombination of functional groups. For example, treatments with sulfuric acid and nitric acid were efficient in improving carboxyl and nitro functional groups of biochar, respectively [112]. After base activation, the content of O-containing functional groups on the surface of the biochar were elevated [113]. The species of surface oxygen were also reshaped. For example, the lactone groups were notably enriched with the treatment of alkaline agents [100]. It was demonstrated that the transition of functionality was responsible for the increase in thermal stability of the alkali-modified biochar [113]. Considering the safety risk of using strong acid and alkali, weak acid and alkali were suggested as possible substitutes. The use of phosphoric acid (H_3PO_4) increased the content of carboxylic and hydroxylic groups and enlarged pore structure by producing water vapor (Formula 1) [114], thereby inducing optimal Cr adsorption capacity [115]. Organic acid, such as acetic acid, oxalic acid, and malic acid, was also observed to stimulate the formation of COOH group on the biochar [116]. However, the interplay between different organic acids and biochars was significantly different. For example, acetic acid efficiently oxidized woody biochars but made no difference to manure-derived biochars [116]. The oxidation ability of manure-derived biochar was significantly improved by oxalic acid [116]. Therefore, it could be concluded that

feedstocks not only influence the characteristics of pristine biochars but also interfere with their modification process. In addition, the introduction of heteroatom N into biochar increased the percentage of carbon-centered persistent free radicals, thereby promoting the reduction of Cr(VI) [117].



The surfactants applied in biochar modification involve cationic, anionic, nonionic, and gemini surfactants. Aside from additional functional groups, surfactants were found to decrease interfacial tension and then facilitate ion exchange. Cetyltrimethyl ammonium bromide, a cation surfactant, enhanced the biochar biosorption of Cr(VI) by additional hydrophilic and hydrophobic groups [63]. The nonionic surfactant Triton X-100, when combined with biochar, improved the fixation of Cr(VI) by adjusting interfacial tension and pH of solution [118]. Under the coexistence of anionic surfactants and biochar, the efficiency of Cr(VI) adsorption was impeded, whereas the rate of Cr(III) removal was accelerated due to the change of surface charge [118].

2.2.4 Biological modification

Biological modification is potential but not widely applied in the preparation of biochar. Contemporary biological modification principally makes use of microbe to reconstruct feedstock structure as a pretreatment method. In recent decades, efforts have been underway to explore possible applications of biological technology in biochar optimization. Although the utilization of fungi in biomass degeneration has been extensively documented [119], there have been few studies conducted to utilize these fungi in biological biochar modification. Anaerobic digestion is a biomass pretreatment approach with anaerobic bacteria [120]. Biochar made from digested residue displayed higher alkalinity, SA, ion exchange abilities, hydrophobicity, and more negative surface charge, as compared to those made from undigested precursors [120]. Similarly, cellulose-degrading microbes have been found to upgrade the adsorption capacity of biochar as a result of the development of pore structures [121]. Higher capacitance and cycling stability were also introduced by the optimized porous

structures and graphitization, which resulted from the depolymerization of lignin-degrading bacterium [122]. This may provide excellent capacity for Cr(VI) adsorption and electron shuttle to immobilize Cr. Apart from being modified prior to carbonization, biochars were also defined as promising inoculum matrices for functional microbes and its metabolites, such as biofilms [123], which significantly improved the efficiency of biological treatment of pollutants. Therefore, the functional microorganisms could be used as modifiers for the improvement of the remediation efficiency of the produced biochar. For example, biochar may be utilized in combination with Cr reducing bacteria, thereby forming a long-acting sustained release material for the remediation of Cr contamination.

2.3 Characteristics

Biochar has relatively high level of SA, CEC, porosity, and functional groups, which are responsible for the sufficient adsorption sites. Mostly, biochar is alkaline, while the pH of some biochars is neutral or even slightly acidic [124]. Despite the common properties discussed above, there are some specific characteristics of biochar attracting growing interests. Based on its redox characteristics, biochar is able to act as electron donor, electron acceptor, and electron shuttle in the redox reaction with Cr and other redox-active substances [125-127]. With the photo irradiation, biochar could reduce Cr(VI) by photogenerated electrons due to its photosensitive characteristics [128, 129]. As the basic physicochemical properties of biochar have been intensively illustrated in various dimensions [22, 33, 46, 49], this section only covers the redox and photosensitive characteristics of biochar.

2.3.1 Redox mediator

Considering different adsorption affinity of biochar to Cr(VI) and Cr(III), the reduction of Cr could trigger a considerable spike in Cr removal. The free radicals, electronical conductive region, and other redox-active moieties in biochar are considered as the major factors that contribute to the redox conversion of contaminants.

The occurrence of reactive oxygen species, particularly persistent free radicals (PFRs) in the transformation of redox-active elements, has drawn a great deal of interest. PFRs are stable metal-radical complexes with long lifetime, ranging from hours to months [130]. PFRs have dissimilar center atoms (*e.g.*, carbon, oxygen, nitrogen, and metals), conferring different capacities of electron donation and subsequent Cr(VI) immobilization [86]. The unpaired electrons contained in these core atoms could be directly transited to Cr(VI) [131] by single-electron transfer [132]. Moreover, PFRs had been observed to serve as electron shuttle between ferric substances and Cr(VI) [125]. Regarding the generation of PFRs in biochar, temperatures and metal loadings exhibited dual effects. The amount of free radicals increased remarkably along with the increase of HTT (up to 500 °C); however, it began to decrease as HTT continued increasing to 700 °C [29, 132]. The correlation between PFR formation and metallic ions (*e.g.*, Fe³⁺, Cu²⁺, Ni²⁺, Co²⁺, and Zn²⁺) was generally positive; however, it turned into negative in biochar with high content of metal [133]. This could be ascribed to the assumption of PFRs as electron shuttles in the reduction of transition metal [134]. The doping of Fe³⁺ ions had higher efficiency than Cu²⁺ in the formation of oxygen-centered PFRs [135]. The quantity and type of PFRs in biochar were altered after pretreatment of phenolic compounds (such as hydroquinone, catechol, and phenol) [133]. Moreover, it was studied that reactive oxygen species, such as H₂O₂ and ·OH, could be produced from the electron transfer between the oxygen and phenolic groups on biochar [136].

Electrical conductivity is another vital indicator to evaluate the redox mediating ability of biochar. The algal- and poultry litter-derived biochar offered comparatively higher levels of electrical conductivity than other lignocellulosic biomass-derived biochars [137]. Generally, the conductive ability of biochar increased with the increase of HTT, owing to the formation of the graphitic region [137]. Fewer exceptions were found in swine solids-derived biochar whose electrical conductivity decreased with the increment of HTT [138]. This might result from the low converting rate of feedstocks into conductive matrices. The conductivity derived from the graphene domain of biochar was found to favor the direct interspecies electron transfer [139]. However, Zhang, et al. [140] proposed that the conductivity was negatively correlated with the efficiency of direct interspecies electron transfer process.

Redox-active functional groups (such as phenolic –OH and quinonyl –C=O) in biochar have been suggested as driving forces behind redox reaction involving electron acceptance, donation, and shuttle [140]. The pattern of electron donating capacity versus HTT showed the inconsistency among various feedstocks. In general, the moieties in biochar prepared by lignocellulosic biomass preferred to be reducible (electron-accepting) rather than oxidizable (electron-donating) with increasing HTT from 200 to 700 °C [141]. At the same calcination temperature, the electron donating capacity of grassy biochar was shown to be higher than that of woody biochar, due to the higher phenolic hydroxyl groups in the former samples [141]. Similarly, bamboo-derived biochar exhibited superior electron donating capacity than pinewood-derived biochar [142]. Therefore, it was determined that the feedstock played a more essential role on electron donating capacity of biochar than temperature. The electron donating capacity of bone-derived biochar was comparable to that of plant biochar, whereas its electron accepting capacity was higher than that of plant biochar [141, 143]. For the total electron transfer, the capacity of sawdust [144], straw [145], and wood-derived biochar [146] increased to a maximum at 500°C and then dropped at higher temperatures. However, the inflection point for bone char was 850 °C [143]. The electron transfer capacity of animal-derived biochar [143] was higher than that of plant-derived biochar [141]. Lignin-derived biochar showed lower electron transfer capacity than biochars derived from hemicellulose and cellulose [142]. The presence of quinone species, quaternary N, and pyridine-N-oxide species also increased the electron accepting capacity of biochar [143], which could bind with CrO_4^{2-} via the covalent bond between the single O atom of CrO_4^{2-} and electron-deficient C atoms [117]. With respect to redox mechanism, phenolic groups (electron donors) were generated under low HTT levels, whereas quinoid moieties (electron acceptors) emerged under moderate and high levels of HTT [141]. Thus, the phenolic group was the major determinant for electron donation and transfer, while the conjugated structure became more prevailing with increasing HTT [147].

2.3.2 Photosensitivity

The photosensitivity of biochar could influence the reduction of Cr(VI). As an economic biomaterial with excellent porosity and stability, biochar has been viewed as the desired carbon matrix to support photosensitive chemicals, such as BiOBr, TiO₂, and C₃N₄ [51, 128, 129]. Generally, PFRs and quinone-like moieties from solid biochar are the main contributors in radical generation under ultraviolet light [148]. The oxygenated functional groups on the biochar surface shifted the excited electrons to the electron acceptor under illumination, thereby producing reactive oxygen species [149]. In modified biochar, the presence of sp²-hybridized structures and graphitic-N groups accelerated Cr(VI) reduction under the visible light condition [150]. The processing of ball milling promoted the development of phenolic moiety and carbon defect, which improved the photocatalytic capacity of biochar [77]. With the excitation of light, more dissolved organic matters were released from biochar through photo-transformation and photo-mineralization [151]. Meanwhile, dissolved biochar was determined to act as photosensitizers [152], facilitating the photocatalytic reduction of Cr(VI) [153]. Dissolved biochar with lower molecular weight showed better potential of photoactivity, in which carbonyl-containing structures accounted for the leading part [152]. The carbonyl groups in dissolved biochar stimulated the generation of singlet oxygen, whereas silica minerals and phenolic groups in solid biochar participated in the production of superoxide [154].

3 Mechanisms involved in the remediation of Cr contamination by biochar

Biochar could be a promisingly efficient agent in Cr decontamination through the adsorption, reduction, electron shuttle, and photocatalysis processes (Fig. 2). Generally, free Cr(VI) ions were reduced at first, and then attached to electronegative surface of biochar via chemisorption [96]. The resultant Cr(III) was retained on the surface by ion exchange, complexation, and precipitation [155]. For some biochar with positively charged surface, Cr(VI) ions were electrostatically attracted, and then reduced to Cr(III) via direct or indirect

pathway [156]. And the Cr(III) may release into environment due to the electrostatic repulsion [155]. These processes of Cr immobilization were summarized as "reduction-adsorption" and "adsorption-reduction-adsorption" pathways. Furthermore, electron shuttle and photocatalysis stimulated by biochar promoted the reduction of Cr(VI) with the presence of redox-active substances, such as iron, lactate, and organic acid with low molecular weight [127, 128, 157]. Phenolic and quinonoid functional groups, free radicals, and graphite constituents in biochar were dominant moieties for Cr(VI) reduction [30, 117]. It's worth noting that modification (*i.e.*, physical, hybrid, chemical, and biological modification) partly changed the pattern of Cr removal by biochar. The newly formed functional groups (such as oxygenic functional groups) on the biochar surface promoted the chemisorption of Cr(VI) [115]. Biochar modified with redox-active metals (*e.g.*, iron and zinc) or nonmetals (*e.g.*, sulfur) reduced Cr(VI) directly [158] or transferring electron from redox mediator to Cr(VI) [81]. The resultant Cr(III) further adsorbed to biochar through forming stable precipitation or complex.

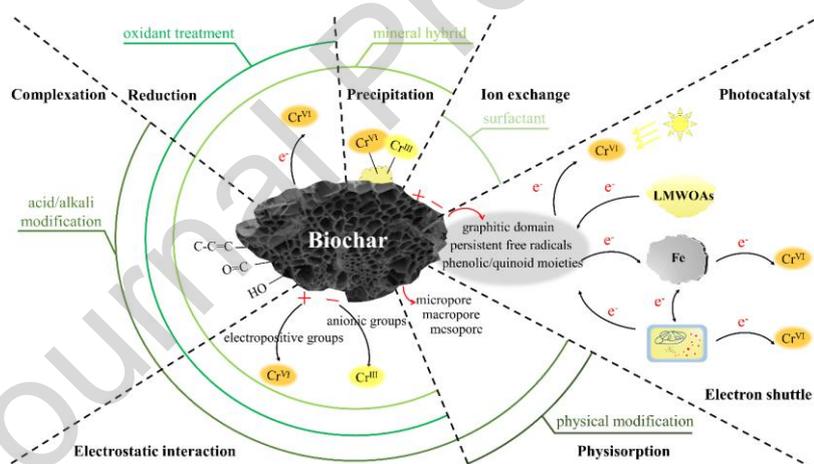


Fig. 2. The mechanisms of Cr decontamination by biochar.

3.1 Adsorbent

Adsorption is the predominant mechanism involved in the remediation of Cr contamination by biochar [156, 159-161]. The Cr adsorptive behavior of biochar involved physical (physisorption and electrostatic interaction) and chemical (ion exchange, surface complexation, and precipitation) reactions. Physisorption is a weak and secondary process that depends on the SA and pore volume [22]. Electrostatic interaction is mainly driven by the

surface charge of biochar and coexisting Cr species, and both of which are controlled by the pH in the environment [36]. Ion exchange is determined by surface functional groups, and usually takes CEC as the major indicator. Complexation (inner- and outer-spheres) forms multi-atom structures (*i.e.*, complexes) via specific metal-ligand interactions, where oxygen functional groups play a crucial role [115].

3.1.1 Pristine biochar as adsorbent

Given the financial efficacy of preparation and subsequent adsorption process, biochar has been well-studied as a desirable and practical adsorbent for Cr removal [30, 33, 155]. These biochars without any modification are featured with high SA and well-distributed pore network. For instance, the SA of woody biochar was reported in the range of 145 to 614 m²·g⁻¹ [67, 162], which was comparable with commercial active carbon. As illustrated in Fig. 3(a), the maximum Cr sorption capacity is not positively related to SA. High HTT improved the SA of biochar but decreased the final Cr(VI) sorption capacity [30], which indicated that SA was not the sole impacting factor determining the Cr(VI) adsorption capacity of biochar. The woody biochar tended to provide higher Cr(VI) adsorption than the grassy one, which might be explained by its relatively high CEC [64] and low pH [48]. The novel precursor, such as sugar beet tailing, showed desirable potential for Cr(VI) and Cr(III) adsorption after pyrolysis, owing to the formation of carboxylic, alcohol and hydroxyl groups [156].

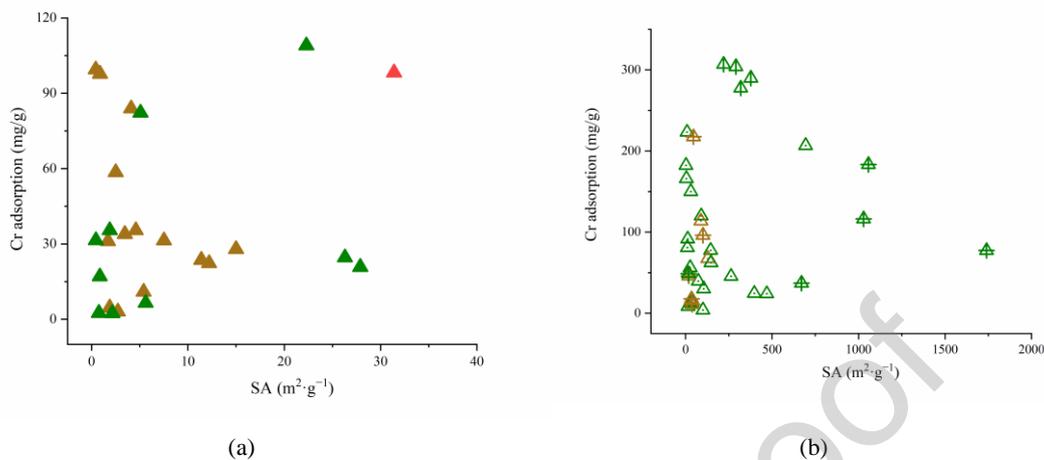


Fig. 3. SA and Cr adsorption of pristine (a) and modified (b) biochars produced from various feedstocks at pyrolysis temperature ranging from 100 to 900 °C. Data are from Table S1 and S2. The solid triangle denotes pristine biochar while interior pattern of dot center, vertical line, and cross denotes biochar modified with metal, surfactant, and acid/alkali, respectively. The color of green, brown, and red represents grass, wood, and sludge derived biochar, respectively.

The value of pH is essential because of its influence on surface charge and functional groups of biochar, as well as on Cr speciation. It has been widely acknowledged that the Cr(VI) is easily removed by pristine biochar in an acid condition [156, 159, 160]. With pH less than pH_{zpc} , the electropositive surface functional groups derived from protonation enhanced the electrostatic attraction to electronegative Cr species [163]. In addition, the positively charged surface reduced the competitive adsorption of OH^- anions and supplied protons for the reduction of Cr(VI) [164]. Thus, biochar fabricated from wood, algae, and switchgrass, with acidic pH levels of 3 to 5.8, was more suitable for Cr(VI) adsorption [165].

The adsorption patterns of biochar on Cr(VI) and Cr(III) species were different. The adsorption capacity of municipal sewage sludge-derived biochar on Cr(III) was twice higher than that on Cr(VI) [166]. This superior retention of Cr(III) was also found in biochars derived from rice husk and solid wastes [60]. The immobilization of Cr(III) by biochar was improved with high pH via two main pathways [56, 167]. Firstly, the increase of negative

charges on biochar promoted the electrostatic adsorption of Cr(III) [56]. Secondly, the hydrolysis of Cr(III) and the dissociation of surface functional groups facilitated the complexation of them [167]. Thus, biochar with abundant acidic functional groups exhibited high Cr(III) adsorption capacity [168]. In addition, the formation of amorphous Cr(III) solids tended to occur under alkaline condition. Surface precipitation and ion exchange were considered as key drivers for the adsorption of Cr(III) by sludge-made biochar [166]. However, Pan, et al. [168] proposed that complexation played an important role in the process of Cr(III) adsorption by straw-derived biochar. Cr(III) ions were primarily adsorbed through electrostatic attraction by anionic groups (*e.g.*, $-\text{C}-\text{OH}$, $\text{C}-\text{O}$, $\text{C}-\text{O}-\text{R}$, and $\text{C}=\text{O}$). Therefore, biochar produced at low temperatures with oxygenated surface functional groups was beneficial for Cr(III) adsorption [155, 169].

3.1.2 Modified biochar as adsorbent

Physically modified biochar mainly improved Cr(VI) sorption through efficient contact with dense biochar particles [170]. With the irradiation of ultrasonication, biochar made by algae showed a two-fold higher Cr(VI) adsorption and a quarter of less equilibrium time than the control [62]. Physical modification could also facilitate Cr(VI) uptake by refashioning functional groups. The ball milling process stimulated the formation of the iron carbide phase, exposition of functional groups, and shrinkage of composite hydrodynamic diameter, which resulted in the improvement of Cr(VI) removal rate [81]. The activation of steam increased the SA and converted the dominant functional groups from aldehydes acid into ethers, esters, and carbonyls, thereby increasing the adsorption of Cr(VI) [171].

Mineral hybrid was one of the most common modification methods of optimizing the Cr adsorption capacity of biochar. On the one hand, mineral loading increased the SA of biochar and thus provided additional adsorption sites for free Cr ions [36, 84]. The formation of nano-MgO on the produced biochar increased the SA by five times, resulting in more than a two-fold increase in Cr adsorption [75]. Similarly, the impregnation of ZnO increased SA by eight times, significantly increasing the Cr sorption capacity of biochar [36]. On the other hand, the modification of metal particles was found to bring about low levels of SA. For example, the

embedding of $\gamma\text{-Fe}_2\text{O}_3$ significantly reduced the SA, which attributed to the clogging of porous structures by thick iron particles [99]. Generally, the Cr(VI) maximum sorption capacity did not increase and even decreased with increasing SA of modified biochars (Fig. 3(b)). It demonstrated that SA could only partly explain the mechanism involved in the Cr(VI) adsorption by modified biochar. Biochar modified with different metallic materials performed different patterns for Cr adsorption. For example, the high positive surface charge on biochar was achieved by the formation of Fe_2O_3 , thereby enhancing the adsorption of anionic Cr species [172]. The electrostatic interaction between Cr(VI) anions and electropositive $\gamma\text{-Fe}_2\text{O}_3$ was identified to be the major mechanism for $\gamma\text{-Fe}_2\text{O}_3$ -soldered biochar [99]. The same predominant mechanism has been confirmed for nZVI-modified biochar [161]. Complexation of Cr with carboxyl and hydroxyl controlled the adsorption of Cr on the surface of MgO-anchored biochar [75]. Cr(VI) was adsorbed through electrostatic interaction in the process of Cr immobilization by ZnO-hybrid biochar. The resultant Cr(III) was immobilized via ion exchange (with Al^{3+} , H^+ , or Zn^{2+}) and complexation [36].

The endowment of O/N/S/P containing functional groups was another popular way of optimizing the surface chemical composition of biochar and subsequently promoting the adsorption of Cr. Compared to other acids, H_3PO_4 had higher ability to promote the physical adsorption, complexation, and electrostatic attraction of Cr(VI) through broadening SA, oxidizing hydroxyl groups, and reducing pH, respectively [74, 115]. In addition, polyethylenimine was used to introduce numerous amino groups into biochar, achieving a much stronger Cr(VI) adsorption capacity than that of the pristine one [173]. This could be explained by the fact that amine groups performed strong chelation with Cr(VI) [124]. The protonation of C–N conducted to abundant positive charges on the surface of N-doping biochars, further promoting the adsorption of Cr(VI) anions [117]. In addition to the increase of nitrogen functional groups, the N-doped biochar produced under NH_3 atmosphere displayed favorable magnetic properties, which assisted further separation and recycling [76].

The adsorption of biochar for Cr(III) species could also be enhanced by the modification with anionic surfactants [118]. Minerals contained in biochar were crucial in Cr(III) adsorption because of their assistance in precipitation [174].

3.1.3 Biological role of adsorbent

Considering its optimum adsorptive capacity, biochar showed a unique impact on biological cycling. For instance, retention of signaling compounds by biochar restricted the intercellular communication and gene expression [175]. Biochar was capable of adsorbing metabolites including amino acids and D-glucose [176], which may interfere with metabolism of Cr reducing microbes. The reductive metabolites were proved to regulate the Cr(VI) reduction of bacteria [177]. Thus, the presence of biochar may disturb microbial Cr(VI) reduction through the adsorption of reductive metabolites. The selective adsorption of these metabolites could regulate the inoculation of diverse microbes and their interaction with biochars. Thus, more attention should be paid to the biological impact of biochar when used as a contaminant adsorbent.

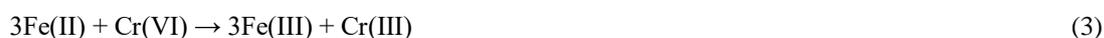
3.2 Reductant

Considering the relationship of valence, adsorption process, and toxicity, the reduction of Cr(VI) to Cr(III) is highlighted in the remediation of Cr contamination [72, 125, 156, 178].

Surface functional groups such as C–O, C–O–C, and O–C–O bonds were important redox-active moieties for Cr(VI) reduction. The carboxyl groups played a dominant role in the reduction of Cr(VI) compared to other surface functional groups [30]. The O atoms in phenol, alcohol, and phosphite served as the major electron donors in Cr(VI) reduction [74]. Biochar extract was proven to reduce Cr(VI) into Cr(III) due to its abundant carboxyl groups and aliphatic carbon [153, 179]. Generally, Cr(VI) reduction by dissolved biochar increased with the decrease of pH [31, 56]. However, the electron donating capacity of dissolved biochar derived from straw was observed to increase with the increase of pH [180]. This might attribute to the high content of humic-like fraction contained in the biochar leachate [181]. Moreover, functional groups in N-doped biochar, such as $-\text{NH}_2$ and $-\text{C}-\text{N}-$, significantly promoted the reduction of Cr(VI) [182].

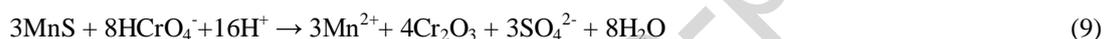
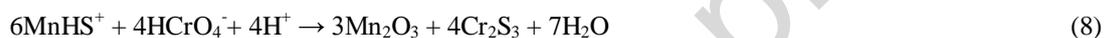
Persistent free radical (PFR) in biochar was another redox-active moiety to stimulate the reduction of Cr(VI) through electron donation. As revealed by electron spin resonance and scavenger experiments, PFRs, such as oxygen-centered PFRs [126], carbon-centered PFRs, and carbon-centered PFRs with an adjacent oxygen atom, could directly donate electron to Cr(VI) [86]. Carbon-centered PFRs showed higher electron donating capacity than carbon-centered PFRs with an adjacent oxygen atom [86]. Additionally, PFRs was found to transfer electrons to molecular oxygen, resulting in superoxide radicals for the reduction of Cr(VI) [183]. The intensity of PFRs increased via the oxidization of phenolic hydroxyl groups by Cr(VI) on the surface of biochar [184]. The variation of HTT, feedstock, and modification altered the generation of PFRs, thereby changing the pattern of Cr(VI) reduction [131, 133]. Biochar modified with iron mineral promoted the electron transfer to Cr(VI) via the formation of PFRs [86]. PFRs reduced Fe(III) into Fe(II) and consequently facilitated the reduction of Cr(VI) [125].

Apart from the improvement of PFRs, the metal-containing materials in biochar could directly participate in the reduction of Cr(VI). Reductive metals such as Fe(0), Fe(II), and Al were common reductive moieties responsible for enhancing Cr(VI) reduction. In the nZVI-modified biochar, Fe(0) species played a limited role on Cr(VI) reduction during the initial period, however, the subsequently generated Fe(II) greatly improved the Cr(VI) reduction (Formula 2–3) [185]. However, Sun, et al. [37] manifested that Fe(0) was the main constituent for Cr(VI) reduction (Formula 4–5). The conversion of Cr(VI) to Cr(III) by Fe(0) species formed FeCr_2O_4 and $\text{Cr}(\text{OH})_3$ on the surface of biochar (Formula 6–7), which were then completely displaced by FeCr_2O_4 with the increasing loading of iron [37]. nZVI was converted into $\gamma\text{-Fe}_2\text{O}_3$ during the process of Cr(VI) reduction [158]. Similarly, Fe_3O_4 loaded on biochar could serve as electron donor for the conversion of Cr(VI) into Cr(III) complexes like CrOOH [186]. Moreover, Fe_3O_4 showed potential attachment of Cr(VI) through chemisorption, thereby enhancing the Cr(VI) reduction by biochar [86].





Furthermore, it was found that biochar extract could dissolve Fe(Mn) oxide, thereby releasing Fe(III) and Mn(II) free ions into environment [187]. The presence of free Fe(III) ions was converted into Fe(II) species by biochar, which consequently reduced Cr(VI) into Cr(III) and formed Cr(III) hydroxides [158]. Therefore, the reduction and adsorption of Cr(VI) species happened simultaneously, as a result of the reducing moieties in biochar [188]. The consequent Cr(III) resided on the surface of biochar by the formation of complexes and precipitations [188]. The similar pathway of Cr(VI) reduction-immobilization was evidenced with the Mn(II) species. Free Mn(II) was oxidized into Mn(III) during the reduction of Cr(VI), forming the precipitation of Mn_2O_3 and Cr_2O_3 (Formula 8–9) [96].



However, the predominant Cr species in MgO-bearing biochar was Cr(VI) rather than Cr(III), which suggested that some metal oxides did not work as reductants as Fe_3O_4 [75].

In addition to metal, nonmetal (*e.g.*, S and Si) containing material was another essential reductive moiety of biochar. The adsorbed Cr(VI) species were reduced by S(II) from dissolved metal sulfide coated on the biochar, resulted in the precipitation of Cr_2S_3 (Formula 8) [96, 101]. Free S(II) ions were converted into S(VI) (Formula 9–10) [96]. The enrichment of silicon in the straw-derived biochar was capable of promoting Cr(VI) reduction. Silicon composition enhanced the attachment of ZVI and iron oxidation, leading to the reduction of Cr(VI) and formation of ferrous chromite (FeCr_2O_4) [41].

3.3 Electron shuttle

It has been verified that the reduction of Cr(VI) can be stimulated by representative electron shuttles in soil [189]. Biochar is a reservoir containing hundreds of micromoles of electrons per gram of mass, which enables biochar to be electron shuttle [190] in the redox reaction of Cr(VI).

Geo-battery [191] and geo-conductor [192] are two main mechanisms for the electron shuttle of biochar, which results from the redox cycle of functional groups and the direct electron transfer of graphic regions, respectively. The contribution of responsible mechanisms in the electron shuttle process depended on the varying degrees of functionality and conjunction in biochars [127]. For example, abundant quinone functional groups on low-HTT biochar were the predominant components supporting electron transfer [147]. With the loss of functionality and the formation of graphic domain, conductivity of the conjugated π -electron system turned into the main driver for the electron shuttle of high-HTT biochar [147]. In general, geo-conductor mechanism was more important than geo-battery for the abiotic electron shuttle by biochar [157]. Based on electrochemical measurements, electron transfer rate of geo-conductor was three times faster than that of geo-battery in biochar [192]. Similarly, with the presence of low molecular weight organic acids (LMWOAs), the electron transfer rate of geo-conductor is much faster than that of geo-battery [127, 193]. Therefore, the electron transfer capacity of biochar for Cr(VI) reduction was positively correlated with HTT, due to the increasing conductivity in carbon matrices [157]. However, the higher contribution of geo-battery than geo-conductor was found in the process of microbial redox transformation when biochar served as the electron shuttle [194]. The value of 20 Å was defined as the maximal distance for the direct electron transfer [195], which implied that the adsorption rather than the diffusion of biochar was of greater importance. For instance, the high affinity of LMWOAs to biochar surface facilitated the geo-conductor electron transfer, and consequently stimulating the reduction of Cr(VI) [127]. The different fractions of biochar possessed distinct electron shuttle capacities. Unlike the key role of dissolved biochar in Cr reduction, leachate from biochar showed a negligible impact on electron shuttle [190]. This discrepancy suggested that the capacities of electron donation and electron transfer may derive from different components of biochar and, thus, should be discussed separately.

Besides aforementioned functional groups and graphic structure, PFR was another major redox mediator for the electron shuttle of biochar. The carbon-centered PFRs produced from Fe₃S₄-hybrid biochar stimulated the cycling of Fe(III)/Fe(II) as electron shuttles, and consequently increased the reduction of Cr(VI) [125]. PFRs in N-doping biochars facilitated

the reduction of Cr(VI) via direct electron transfer instead of transiting electron to anion $O_2^{\cdot-}$ [117]. Semiquinone-type PFRs in a pristine biochar was observed to promote the reduction of Cr(VI) by electron shuttle [164]. Nevertheless, some biochars without modification exhibited inhibitory effect on Cr(VI) reduction. Pristine biochar was determined to activate H_2O_2 , forming $\cdot OH$ through single-electron transit from PFRs to H_2O_2 [196], thereby decreasing the reduction of Cr(VI) [197]. Similarly, persulfate was found to be activated by pristine biochar, thereby generating $SO_4^{\cdot-}$ by transferring one electron from the PFRs to $S_2O_8^{2-}$ [133], which oxidized Cr(VI) to Cr(III) [198].

LMWOAs are common redox-active components in soil [199]. Biochar shuttles electrons between the LMWOAs and Cr(VI) in soil through two pathways [127]. High-HTT pristine biochar mainly served as a geo-conductor after LMWOAs adsorbed on its surface. While geo-battery mechanism dominated the redox reaction of Cr due to high content of oxygenic functional groups on the low-HTT biochar [127]. Moreover, the nanoscale Ag-coated biochar exhibited preferential electron transfer between Cr(VI) and formic acid, which was mainly attributed to the catalytic sites on nano Ag particles [200]. Lactate was a weak electron donor. The co-presence of biochar and lactate showed 1.30 to 17.3 times higher Cr(VI) reduction rate than that of the biochar alone [157]. This indicated that the effect of biochar as an electron shuttle, was much more prominent than being an electron donor in the remediation of Cr contamination. Additionally, the property of biochar as electron shuttle could indirectly influence Cr immobilization by engaging in biogeochemical cycling of iron. The iron oxidation was suppressed by biochar through its negative effect on the growth of the photosynthetic microorganisms [201]. In addition, biochar was able to accept electrons from the biotical source (*e.g.*, iron reducing microorganism) and then donate them to the iron mineral, thereby stimulating the bioreduction rate of the insoluble iron [190, 202]. The mineralogy of microbially reductive product was converted from magnetite (Fe_3O_4) into siderite ($FeCO_3$) by the mediation of biochar [190], which may change the fate of Cr ions. However, Wu, et al. [203] proposed that the transition of mineral product was inhibited by biochar, which might be caused by the adsorption of Fe(II). Also, iron species released from clay minerals were able to serve as electron shuttles in the reduction of Cr(VI) [8]. Therefore,

the biochar modified by iron-containing minerals might be taken as the superior electron shuttle for the improvement of the Cr(VI) reduction. Several researches have demonstrated that electron shuttle improved the efficiency of Cr reduction using bacteria through facilitating the extracellular electron transfer [17, 204]. Moreover, biochar was utilized as electron shuttle to facilitate the reduction of oxygen in microbial fuel cells for Cr(VI) reduction because of its high conductivity [205].

3.4 Photocatalyst

Biochar as carbon skeleton facilitated electron transfer, adherence of photocatalysts, and adsorption of contaminants [206]. The supplementation of biochar favored the adsorption of Cr(VI) to photocatalyst due to its high SA, which facilitated Cr(VI) reduction through its enhanced connection with photogenerated electrons [128]. The well-distributed graphitic structures of biochar matrix accelerated the electron transfer, leading to the ideal photocatalytic reduction of Cr(VI) [51]. The coating of Bi_2WO_6 improved the electrical conductivity of modified biochar, thereby accelerating the migration of photogenerated electron to Cr(VI) [207]. In addition, the Fe in the magnetic biochar was investigated to lower the binding energy of noble metal nanoparticles, increasing the catalytic activity in the reduction process [206, 208]. ZnO [94], ZnFe_2O_4 [209], and $\beta\text{-FeOOH}$ [210] nanoparticles embedded on biochar were identified to serve as photocatalyst, thereby facilitating the reduction of Cr(VI) by photogenerated electrons. The B–H functional groups contained in ZnFe_2O_4 -modified biochar also contributed to the reduction of Cr(VI) [39]. In N-doping biochar, the carbon sp^2 -hybridized structures in oxygen functional groups were excited to produce photogenerated electrons, which accelerated Cr(VI) reduction under visible light condition [150]. Considering the photosensitivity of biochar, it could be deduced that pristine biochar may have the potential to participate in Cr(VI) reduction as a photocatalyst. The dissolved biochars were capable of complexing with Fe(III) and then being photo-excited, thereby indirectly assisting Cr(VI) reduction [153]. Further studies are still required for the illustration of underlying mechanism and application of photocatalysis.

4 Biochar-assisted Cr immobilization with interfering species in actual contaminated environment

4.1 Interaction between biochar and interfering species in Cr-contaminated wastewater

In an actual aquatic Cr-contaminated environment, reaction parameters (adsorbent dosage, pH range, contact time, illumination, *etc.*) and interfering species (ions, organic contaminants, *etc.*) played essential roles in biochar application.

Table S1 and S2 summarized that the acidic environment is preferable for biochar to extract Cr from wastewater. The positively charged surface displayed high adsorption to CrO_4^{2-} through the protonation of functional groups under low pH [163]. Biochar derived from tree leaves, algae, and switchgrass was more constructive to lower-pH environment than sludge-derived biochar [124, 165]. With higher adsorbent dosage, biochar showed superior adsorption efficiency and lower Cr adsorption capacity [36, 211]. At a high initial Cr(VI) concentration, the Cr(VI) adsorption rate of biochar decreased while the adsorption capacity increased [28]. The equilibrium time of Cr sorption differed in biochar produced with different feedstocks [59]. The fine biochar (particle size ranging from 0.15 to 0.5 mm) showed higher rate and quantity of Cr adsorption than the coarse one (0.50 to 1.00 mm) [169]. Moreover, the increasing temperature of adsorption slightly fortified the Cr(VI) adsorption by biochar whereas high temperature ($> 25\text{ }^\circ\text{C}$) reduced the adsorption capacity [63]. However, some researchers demonstrated a constantly promoting effect of rising temperature on Cr(VI) removal efficiency (10 to $45\text{ }^\circ\text{C}$) [38, 188, 211]. Interestingly, the Cr(VI) reduction by biochar was improved in ice due to the freeze concentration effect in the grain boundary [178]. In addition, some other reacting parameters which influenced the redox-active and photosensitive properties of biochar has been evaluated recently. The presence of electron donors, such as lactate, increased the remediation efficiency through mediating Cr(VI) reduction by the biochar [157]. Moreover, the Cr(VI) removal rate was facilitated by illumination, based on the photocatalysis of biochar [39].

Cr species commonly coexist with anionic/cationic background ions and organic contaminants in contaminated water. Generally, the addition of cation, such as K^+ , Na^+ , and Ca^{2+} , was able to neutralize the charged surface of biochar, thereby promoting its electrostatic interaction with Cr(VI) [75, 211]. The co-presence of biochar and anions, such as NO_3^- , HPO_4^{2-} , HCO_3^- , and F^- , competed for the adsorptive sites with anionic Cr species [75, 126]. The competitiveness of the multivalent anions, such as CO_3^{2-} , PO_4^{3-} , SO_4^{2-} , and SeO_4^{2-} , was stronger than that of the monovalent anions, such as Cl^- and NO_3^- [76, 125, 212]. In addition, the inhibitive impact of anions towards Cr(VI) adsorption became apparent with the ascending ionic strength, which was caused by the decreasing activity coefficient of Cr(VI) [99]. However, not all the Cr(VI) adsorption performance of biochar was suppressed by the anionic ions. The existence of nitrate showed minimal impact on the Cr(VI) adsorption of Fe_3O_4 and Mg/Al hydroxide-modified biochar [86, 98]. The presence of NO_3^- and SO_4^{2-} made a negligible difference on the Cr(VI) removal rate of the pristine straw-derived biochar [126]. Moreover, the positive effect of SO_4^{2-} had been found in the adsorption of Cr by a nZVI-modified biochar, which was attributed to the reactive sites on the nZVI surface caused by promoting corrosion [102]. The competitive adsorption of CO_3^{2-} on the biochar was reduced after the modification with HNO_3 [126]. Therefore, the distinct capacity of selective adsorption of Cr(VI) was closely related to the functional groups on the biochar surface. For cationic background ions, Cu^{2+} and Pb^{2+} stimulated the Cr(VI) adsorption on biochar surface as a cation bridge [211, 212]. In contrast, Cu^{2+} and Pb^{2+} substantially inhibited Cr(III) adsorption through the competition for ion-exchange sites on biochar [211, 213]. Moreover, other redox sensitive elements such as Fe, Mn, and As should be taken into consideration due to the redox sensitivity. Surprisingly, Mn(II) inhibited the removal of Cr(VI) [92] while iron ions showed a negligible impact on Cr(VI) removal by pristine biochar [178]. As(III) oxidation was found to facilitate the Cr(VI) reduction of dissolved biochar via electron donation [31]. In contrast, As(V) inhibited the Cr(VI) removal [92]. In the binary system of the Cr species and interfering organic compounds, different patterns of Cr removal have been observed. The concurrence of benzoic acid facilitated the Cr(VI) removal by reducing Cr(VI) into Cr(III) [214]. The hydroxyl groups of biochar bonded with Cr(VI)/Cr(III) and atrazine through inner complex and H-bond, respectively. Thus, the coexistence of atrazine had a

negligible influence on Cr adsorption of the biochar [215]. The removal of Cr(III) was facilitated through the generation of the metal-organic complex in the presence of bisphenol A [216]. However, the introduction of nonpolar hydrophobic organic contaminants limited the adsorption of hydrophilic Cr(VI) ions due to the increasing hydrophobicity of the biochar [115]. Moreover, the anionic orange-type dyes (*i.e.*, methyl orange, orange II, and orange G) lowered the adsorption of CrO_4^{2-} on the Mg–Al-layered double hydroxide [217]. Hence, it could be speculated that anionic organic contaminants may compete with Cr(VI) in the adsorption process of biochar. With the irradiation of UV, orange G could serve as electron donor, promoting the reduction of Cr(VI) by biochar [129]. Similarly, synergistic impact has been observed under the co-presence of Cr(VI) and 4-fluorophenol, which resulted from the photocatalytic effect of biochar [128].

In summary, recent studies mainly analyzed the effect of interfering environmental factors on Cr removal by biochar in a single simulating system. Although some studies have utilized NaNO_3 and Na_2SO_4 as background electrolytes [185], only the few have discussed the application of biochar in actual Cr contaminated wastewater [74, 178, 218]. In addition to Cr species, heavy metal (*e.g.*, Mn^{2+} , Zn^{2+} , Cu^{2+} , and Pb^{2+}) and organic contaminants were found to contain in real wastewater, thereby influencing the practical use of biochar.

4.2 Interaction between biochar and interfering species in Cr-contaminated soil

4.2.1 Biochar-assisted Cr immobilization changes the properties of soil, microbe, and plant

Biochar has been reported to ameliorate soil properties via different ways. The structure of soil was refined through increasing aeration and reducing soil tensile strength by biochar [219]. Soil pH and CEC were elevated due to the alkaline matrix and H^+ adsorption of biochar [43, 220, 221]. The adsorption of organic substance and metal to biochar could improve the texture of soil [222]. A variety of biochar has been applied in the remediation of Cr

contaminated soil. Compared to straw and wood-derived biochar, sugarcane bagasse-derived biochar possessed higher Cr(VI) immobilization capacity in soil, mainly due to its low pH (< 6.5) [223-225]. Moreover, biochar prepared under low HTT had relatively high functionality, which was beneficial for the adsorption of Cr [223]. Hybrid modification with reductive metal material, such as nZVI, promoted the immobilization of Cr(VI) by biochar via enhanced reduction and electron shuttle [109, 226, 227]. The introduction of clay nanoparticle enhanced the Cr(VI) immobilization capacity of biochar by providing active adsorption sites in alkaline soil [228]. In addition to direct impact on soil properties, the supplementation of biochar influenced the activity of microbe and plant, thereby assisting the immobilization of Cr in soil indirectly [220].

The microbial abundance and community structure in soil were reshaped after inoculation of biochar [24]. For instance, biochar derived from feedstocks with higher lignocellulosic content (*e.g.*, wood) showed more positive influence on microbial population density than those derived from manure or crop residue [222]. The possible roles of biochar in microbial activity are presented herein. First, biochar could act as microbial shelter. Bacteria could adhere to biochar instead of being leached out while this promoting effect was not obvious for fungi [220]. The application of biochar facilitated the genetic abundance of soil bacteria; however, it restricted that of fungi [229]. It should be noted that biochar-dwelling microbes maybe unable to significantly grow in a relatively short term (<3 years), owing to the low carbon availability and small pores of biochar [230]. Second, biochar could act as nutrient pool. The labile composition leached from biochar might be utilized by microbes as a nutrient source. However, whether or not the nutrients supplied by biochar facilitated microbial biomass was still unclear [220]. Third, biochar could act as a redox mediator. The quinone moiety of biochar was responsible for the electron acceptance, donation, and shuttle in the microbial processes of iron reduction, acetate oxidation, and nitrate reduction, respectively [190, 194]. Lastly, biochar could act as Cr adsorbent. The Cr adsorption of biochar could offset the detrimental impact on soil microbe caused by Cr contamination [13]. It has been observed that the microbial activity in soil was positively correlated with the Cr adsorption capacity of biochar [231]. In a pragmatic application, the copresence of Cr-

reducing bacteria and biochar efficiently reduced Cr phytotoxicity and brought about physiological benefits [232].

Due to the change of physicochemical and biological properties of soil, the response of plants to Cr contamination also varied with the addition of biochar. The nutrition and biomass of fruits were upgraded by biochar [233]. The plant tolerance towards Cr was improved due to the positive role of biochar on antioxidative enzymes [234]. The uptake and bioaccumulation of Cr in plants were reduced by the supplementation of biochar [14, 221, 235]. Biochar also facilitated the activities of soil dehydrogenase, β -glucosidase, and urease, thereby increasing metabolism and activate microbial community [236]. Accordingly, biochar could potentially ameliorate the toxic stress of Cr on plants by optimizing soil enzymes activities, facilitating plant physiological functions, and changing metal transport patterns in the soil-plant system [224].

4.2.2 Different soil conditions influence biochar-assisted Cr immobilization

After applied into the soil, the properties of biochar were changed by soil compositions including clay, iron mineral, and organic matter [237]. This process was summarized as biochar aging [238]. Aging introduced oxygenated groups, especially hydrophilic functional groups (such as carboxylic and phenolic groups) onto the surface of biochar [238, 239]. This oxidation phenomenon was more evident in acid soil than the soil with high pH [238]. The additional O-containing functional groups provided potential adsorption sites for Cr species [223]. Moreover, the adsorption of Cr(VI) might be promoted in acidic environment caused by the reduced alkalinity of aged biochar [239].

The increasing O-containing functional groups of the aged biochar may directly attach to soil minerals [240]. For example, organometallic complexes were formed on the biochar surface after incubation with representative clay minerals, such as montmorillonite and kaolinite. These complexes increased the SA as well as the resistance of biochar towards oxidation [241, 242]. Therefore, biochar would be stable and, thus, have a long interacting

period, when applied to soil with high mineral content. In contrast, the iron minerals, such as hematite and goethite, oxidized the reductive functional groups and blocked the surface, thereby significantly reducing the Cr(VI) reduction rate of biochar [243].

Likewise, organic matters showed dual interfering impacts on Cr(VI)-contaminated soil amended with biochar. For one thing, humic substances reduced the SA of biochar by surface coverage and pore-filling effect [162], which may hamper the sorption of Cr(VI) by biochar. For another thing, the humic acid promoted the reduction of Cr(VI) by transferring electron between biochar and Cr(VI) ions [211].

In the soils of different land-use types, biochar exhibited different rates of mineralization, contributing to the diverse indigenous microbial communities [219]. Biochar possessed a more desirable Cr(VI) reduction in acidic soil than in neutral soil [109]. In the long term, the aged biochar that was synthesized with different temperatures and feedstocks showed contradictory impacts on contaminant adsorption [242] and metal(loid)s speciation [237]. To conclude, biochar-assisted Cr immobilization in soil varied depending on different types of plants, microbes, soils, and biochars.

5 Further perspectives

The remediation of Cr contamination by biochar are confronted with special challenges. The general properties of biochar have been well-studied, however, the redox-active and photocatalytic properties of biochars are not widely investigated. The studies of quantifying their potential role as electron shuttle or photocatalyst are limited. The electron transfer pathways of biochar in Cr immobilization are also unclear. Future studies need to be conducted to provide an insight into electron transfer mechanism for Cr immobilization.

In acidic and neutral environment, biochars exhibited a more stable adsorption to Cr(VI) than other adsorbents such as nanoparticles [169]. However, Cr ions adsorbed on biochars may desorb under alkaline condition, thereby posing a potential environmental threat [169]. Biochar exhibited higher desorption rate for Cr(VI) than Cr(III) due to its limited electrostatic interaction with Cr(VI) [60]. In addition, the secondary pollution caused by biochar

(especially modified biochar) should be taken into consideration. Heavy metals contained in precursor (*e.g.*, sludge) may be accumulated during pyrolysis and released into environment in following application [43]. The volatile organic compounds and free radicals contained in biochar may be inhibitory for microbial growth and plant germination [130]. Moreover, PFRs may interact with coexisted contaminants, resulting in unpredictable secondary contamination. The change of biochar properties caused by aging process further complexed the generation of secondary contamination. Therefore, the stability of biochar should be evaluated before its application.

Thus far, studies about the biochar remediation of Cr contamination are still limited in a laboratory scale. The capacity of biochar on Cr stabilization is investigated under simulated system, which is unable to provide support for further practical application. Hence, field and commercial-scale applications are necessary. Considering the complexity of various environmental variables (*e.g.*, organic matter and soil mineral), the fate of biochar and its subsequent effects on contaminants in the long term presents a critical research gap and requires further studies.

6 Conclusions

In conclusion, we have presented an overview of the preparation and characterization of biochar, summarizing its mechanism and application in the remediation of Cr contamination. Besides feedstock and HTT, the characteristics of biochar vary with different modifications including hybrid, chemical, physical, and biological methods. The optimization of pyrolysis conditions and manipulation of designated biochar are critical for the improvement of Cr removal efficiency. In the remediation process, "reduction-adsorption" and "adsorption-reduction-adsorption" are the two main Cr immobilization pathways. Cr(III) was stabilized as complexes or precipitations. In addition, electron shuttle participates in the transformation of Cr via geo-battery and geo-conductor mechanisms. Functional groups, graphic structures, and PFRs are the predominant redox-active moieties in the process of electron transfer. Furthermore, the reduction of Cr(VI) is facilitated by photocatalysis based on photosensitivity of biochar. Biochar plays an important role in the soil-plant-microbe system. When applied

into soil, biochar may age via abiotic and biotic ways, altering the biochar properties and subsequent influence on Cr immobilization. Interfering species in Cr wastewater change the properties of biochar and its Cr removal capacity. Application of biochar for Cr immobilization in real environment needs further investigation.

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References

- [1] J. Liu, N. Li, W. Zhang, X. Wei, D.C.W. Tsang, Y. Sun, X. Luo, Z.a. Bao, W. Zheng, J. Wang, G. Xu, L. Hou, Y. Chen, Y. Feng, Thallium contamination in farmlands and common vegetables in a pyrite mining city and potential health risks, *Environmental Pollution*, 248 (2019) 906-915.
- [2] J. Liu, X. Luo, Y. Sun, D.C.W. Tsang, J. Qi, W. Zhang, N. Li, M. Yin, J. Wang, H. Lippold, Y. Chen, G. Sheng, Thallium pollution in China and removal technologies for waters: A review, *Environment International*, 126 (2019) 771-790.
- [3] J. Liu, X. Wei, Y. Zhou, D.C.W. Tsang, Z.a. Bao, M. Yin, H. Lippold, W. Yuan, J. Wang, Y. Feng, D. Chen, Thallium contamination, health risk assessment and source apportionment in common vegetables, *Science of The Total Environment*, 703 (2020) 135547.
- [4] J. Liu, M. Yin, T. Xiao, C. Zhang, D.C.W. Tsang, Z.a. Bao, Y. Zhou, Y. Chen, X. Luo, W. Yuan, J. Wang, Thallium isotopic fractionation in industrial process of pyrite smelting and environmental implications, *Journal of Hazardous Materials*, 384 (2020) 121378.
- [5] J. Wang, Y. Jiang, J. Sun, J. She, M. Yin, F. Fang, T. Xiao, G. Song, J. Liu, Geochemical transfer of cadmium in river sediments near a lead-zinc smelter, *Ecotoxicology and Environmental Safety*, 196 (2020) 110529.
- [6] Y. Xiang, X. Yang, Z. Xu, W. Hu, Y. Zhou, Z. Wan, Y. Yang, Y. Wei, J. Yang, D.C.W. Tsang, Fabrication of sustainable manganese ferrite modified biochar from vinasse for enhanced adsorption of fluoroquinolone antibiotics: Effects and mechanisms, *Science of The Total Environment*, 709 (2020) 136079.
- [7] M. Shahid, S. Shamshad, M. Rafiq, S. Khalid, I. Bibi, N.K. Niazi, C. Dumat, M.I. Rashid, Chromium speciation, bioavailability, uptake, toxicity and detoxification in soil-plant system: A review, *Chemosphere*, 178 (2017) 513-533.
- [8] S. Kwak, J.-C. Yoo, D.H. Moon, K. Baek, Role of clay minerals on reduction of Cr(VI), *Geoderma*, 312 (2018) 1-5.
- [9] L. Keith, W. Telliard, ES&T Special Report: Priority pollutants: I-a perspective view, *Environmental Science & Technology*, 13 (1979) 416-423.
- [10] W.H. Organization, Guidelines for drinking-water quality, in, World Health Organization, 2017, pp. 631.

- [11] J. Kotaś, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, *Environmental Pollution*, 107 (2000) 263-283.
- [12] R.K. Tandon, P.T. Crisp, J. Ellis, R.S. Baker, Effect of pH on chromium(VI) species in solution, *Talanta*, 31 (1984) 227-228.
- [13] G. Choppala, N. Bolan, A. Kunhikrishnan, R. Bush, Differential effect of biochar upon reduction-induced mobility and bioavailability of arsenate and chromate, *Chemosphere*, 144 (2016) 374-381.
- [14] A. Kumar, S. Joseph, L. Tsechansky, I.J. Schreiter, C. Schüth, S. Taherysoosavi, D.R.G. Mitchell, E.R. Graber, Mechanistic evaluation of biochar potential for plant growth promotion and alleviation of chromium-induced phytotoxicity in *Ficus elastica*, *Chemosphere*, 243 (2020) 125332.
- [15] F. Zhao, Y. Liu, S. Ben Hammouda, B. Doshi, N. Guijarro, X. Min, C.-J. Tang, M. Sillanpaa, K. Sivula, S. Wang, MIL-101(Fe)/g-C₃N₄ for enhanced visible-light-driven photocatalysis toward simultaneous reduction of Cr(VI) and oxidation of bisphenol A in aqueous media, *Applied Catalysis B-Environmental*, 272 (2020).
- [16] Y. Gong, D. Zhao, Q. Wang, An overview of field-scale studies on remediation of soil contaminated with heavy metals and metalloids: Technical progress over the last decade, *Water Research*, 147 (2018) 440-460.
- [17] J.K. Fredrickson, H.M. Kostandarithes, S.W. Li, A.E. Plymale, M.J. Daly, Reduction of Fe(III), Cr(VI), U(VI), and Tc(VII) by *Deinococcus radiodurans* R1, *Appl Environ Microbiol*, 66 (2000) 2006-2011.
- [18] K. GracePavithra, V. Jaikumar, P.S. Kumar, P. SundarRajan, A review on cleaner strategies for chromium industrial wastewater: Present research and future perspective, *Journal of Cleaner Production*, 228 (2019) 580-593.
- [19] R. Jobby, P. Jha, A.K. Yadav, N. Desai, Biosorption and biotransformation of hexavalent chromium [Cr(VI)]: A comprehensive review, *Chemosphere*, 207 (2018) 255-266.
- [20] J. Lehmann, S. Joseph, Biochar for environmental management: an introduction, in: *Biochar for environmental management*, Routledge, 2015, pp. 33-46.
- [21] H. Wang, H. Deng, Y. He, L. Huang, D. Wei, T. Hao, S. Wang, L. Jin, L. Zhang, Facile and sustainable synthesis of slit-like microporous N-doped carbon with unexpected electrosorption performance, *Chemical Engineering Journal*, 396 (2020).
- [22] X.D. Yang, Y.S. Wan, Y.L. Zheng, F. He, Z.B. Yu, J. Huang, H.L. Wang, Y.S. Ok, Y.S. Jiang, B. Gao, Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review, *Chemical Engineering Journal*, 366 (2019) 608-621.
- [23] L. Luo, C. Xu, Z. Chen, S. Zhang, Properties of biomass-derived biochars: Combined effects of operating conditions and biomass types, *Bioresour Technol*, 192 (2015) 83-89.
- [24] T. Bandara, A. Franks, J.M. Xu, N. Bolan, H.L. Wang, C.X. Tang, Chemical and biological immobilization mechanisms of potentially toxic elements in biochar-amended soils, *Critical Reviews in Environmental Science and Technology*, 50 (2019) 1-76.
- [25] X. Cao, J.J. Pignatello, Y. Li, C. Lattao, M.A. Chappell, N. Chen, L.F. Miller, J. Mao, Characterization of Wood Chars Produced at Different Temperatures Using Advanced Solid-State ¹³C NMR Spectroscopic Techniques, *Energy & Fuels*, 26 (2012) 5983-5991.
- [26] D. Kołodyńska, J. Krukowska, P. Thomas, Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon, *Chemical Engineering Journal*, 307 (2017) 353-363.
- [27] S. Richards, J. Dawson, M. Stutter, The potential use of natural vs commercial biosorbent material

to remediate stream waters by removing heavy metal contaminants, *Journal of Environmental Management*, 231 (2019) 275-281.

[28] J. Zhang, S. Chen, H. Zhang, X. Wang, Removal behaviors and mechanisms of hexavalent chromium from aqueous solution by cephalosporin residue and derived chars, *Bioresource Technology*, 238 (2017) 484-491.

[29] D. Zhong, Y. Jiang, Z. Zhao, L. Wang, J. Chen, S. Ren, Z. Liu, Y. Zhang, D.C.W. Tsang, J.C. Crittenden, pH Dependence of Arsenic Oxidation by Rice-Husk-Derived Biochar: Roles of Redox-Active Moieties, *Environmental Science & Technology*, 53 (2019) 9034-9044.

[30] X. Zhang, W. Fu, Y. Yin, Z. Chen, R. Qiu, M.O. Simonnot, X. Wang, Adsorption-reduction removal of Cr(VI) by tobacco petiole pyrolytic biochar: Batch experiment, kinetic and mechanism studies, *Bioresour Technol*, 268 (2018) 149-157.

[31] X. Dong, L.Q. Ma, J. Gress, W. Harris, Y. Li, Enhanced Cr(VI) reduction and As(III) oxidation in ice phase: important role of dissolved organic matter from biochar, *J Hazard Mater*, 267 (2014) 62-70.

[32] L. He, H. Zhong, G. Liu, Z. Dai, P.C. Brookes, J. Xu, Remediation of heavy metal contaminated soils by biochar: Mechanisms, potential risks and applications in China, *Environmental Pollution*, 252 (2019) 846-855.

[33] H. Li, X. Dong, E.B. da Silva, L.M. de Oliveira, Y. Chen, L.Q. Ma, Mechanisms of metal sorption by biochars: Biochar characteristics and modifications, *Chemosphere*, 178 (2017) 466-478.

[34] C. Zhang, B. Shan, Y. Zhu, W. Tang, Remediation effectiveness of *Phyllostachys pubescens* biochar in reducing the bioavailability and bioaccumulation of metals in sediments, *Environmental Pollution*, 242 (2018) 1768-1776.

[35] Y.M. Zhou, B. Gao, A.R. Zimmerman, J. Fang, Y.N. Sun, X.D. Cao, Sorption of heavy metals on chitosan-modified biochars and its biological effects, *Chemical Engineering Journal*, 231 (2013) 512-518.

[36] Y. Shi, R. Shan, L. Lu, H. Yuan, H. Jiang, Y. Zhang, Y. Chen, High-efficiency removal of Cr(VI) by modified biochar derived from glue residue, *Journal of Cleaner Production*, 254 (2020) 119935.

[37] Y. Sun, I.K.M. Yu, D.C.W. Tsang, X. Cao, D. Lin, L. Wang, N.J.D. Graham, D.S. Alessi, M. Komarek, Y.S. Ok, Y. Feng, X.D. Li, Multifunctional iron-biochar composites for the removal of potentially toxic elements, inherent cations, and hetero-chloride from hydraulic fracturing wastewater, *Environ Int*, 124 (2019) 521-532.

[38] C. Li, L. Zhang, Y. Gao, A. Li, Facile synthesis of nano ZnO/ZnS modified biochar by directly pyrolyzing of zinc contaminated corn stover for Pb(II), Cu(II) and Cr(VI) removals, *Waste Manag*, 79 (2018) 625-637.

[39] Y. Yu, Q. An, L. Jin, N. Luo, Z. Li, J. Jiang, Unraveling sorption of Cr (VI) from aqueous solution by FeCl₃ and ZnCl₂-modified corn stalks biochar: Implicit mechanism and application, *Bioresource Technology*, 297 (2020) 122466.

[40] Y.Q. Yi, G.Q. Tu, D.Y. Zhao, P.E. Tsang, Z.Q. Fang, Biomass waste components significantly influence the removal of Cr(VI) using magnetic biochar derived from four types of feedstocks and steel pickling waste liquor, *Chemical Engineering Journal*, 360 (2019) 212-220.

[41] L. Qian, X. Shang, B. Zhang, W. Zhang, A. Su, Y. Chen, D. Ouyang, L. Han, J. Yan, M. Chen, Enhanced removal of Cr(VI) by silicon rich biochar-supported nanoscale zero-valent iron, *Chemosphere*, 215 (2019) 739-745.

[42] Y.F. Shen, Carbothermal synthesis of metal-functionalized nanostructures for energy and environmental applications, *J Mater Chem A*, 3 (2015) 13114-13188.

- [43] E. Agrafioti, G. Bouras, D. Kalderis, E. Diamadopoulos, Biochar production by sewage sludge pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 101 (2013) 72-78.
- [44] Y. Qin, L. Zhang, T. An, Hydrothermal Carbon-Mediated Fenton-Like Reaction Mechanism in the Degradation of Alachlor: Direct Electron Transfer from Hydrothermal Carbon to Fe(III), *ACS Appl Mater Interfaces*, 9 (2017) 17115-17124.
- [45] O.R. Harvey, B.E. Herbert, L.-J. Kuo, P. Louchouart, Generalized Two-Dimensional Perturbation Correlation Infrared Spectroscopy Reveals Mechanisms for the Development of Surface Charge and Recalcitrance in Plant-Derived Biochars, *Environmental Science & Technology*, 46 (2012) 10641-10650.
- [46] A. Mukherjee, A.R. Zimmerman, W. Harris, Surface chemistry variations among a series of laboratory-produced biochars, *Geoderma*, 163 (2011) 247-255.
- [47] J. Jin, Y. Li, J. Zhang, S. Wu, Y. Cao, P. Liang, J. Zhang, M.H. Wong, M. Wang, S. Shan, P. Christie, Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge, *Journal of Hazardous Materials*, 320 (2016) 417-426.
- [48] F. Ronsse, S. van Hecke, D. Dickinson, W. Prins, Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions, *Gcb Bioenergy*, 5 (2013) 104-115.
- [49] F. Lian, B. Xing, Black Carbon (Biochar) In Water/Soil Environments: Molecular Structure, Sorption, Stability, and Potential Risk, *Environ Sci Technol*, 51 (2017) 13517-13532.
- [50] F.-X. Collard, J. Blin, A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin, *Renewable and Sustainable Energy Reviews*, 38 (2014) 594-608.
- [51] A. Geng, L. Xu, L. Gan, C. Mei, L. Wang, X. Fang, M. Li, M. Pan, S. Han, J. Cui, Using wood flour waste to produce biochar as the support to enhance the visible-light photocatalytic performance of BiOBr for organic and inorganic contaminants removal, *Chemosphere*, 250 (2020) 126291.
- [52] Y.-l. Zhang, W.-g. Wu, S.-h. Zhao, Y.-f. Long, Y.-h. Luo, Experimental study on pyrolysis tar removal over rice straw char and inner pore structure evolution of char, *Fuel Processing Technology*, 134 (2015) 333-344.
- [53] P. Fu, S. Hu, L. Sun, J. Xiang, T. Yang, A. Zhang, J. Zhang, Structural evolution of maize stalk/char particles during pyrolysis, *Bioresource Technology*, 100 (2009) 4877-4883.
- [54] H.P. Yang, R. Yan, H.P. Chen, D.H. Lee, C.G. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel*, 86 (2007) 1781-1788.
- [55] X. Qu, H. Fu, J. Mao, Y. Ran, D. Zhang, D. Zhu, Chemical and structural properties of dissolved black carbon released from biochars, *Carbon*, 96 (2016) 759-767.
- [56] L. Qian, W. Zhang, J. Yan, L. Han, W. Gao, R. Liu, M. Chen, Effective removal of heavy metal by biochar colloids under different pyrolysis temperatures, *Bioresour Technol*, 206 (2016) 217-224.
- [57] L. Luo, Z. Chen, J. Lv, Y. Cheng, T. Wu, R. Huang, Molecular understanding of dissolved black carbon sorption in soil-water environment, *Water Res*, 154 (2019) 210-216.
- [58] S. Pap, V. Bezanovic, J. Radonic, A. Babic, S. Saric, D. Adamovic, M. Turk Sekulic, Synthesis of highly-efficient functionalized biochars from fruit industry waste biomass for the removal of chromium and lead, *Journal of Molecular Liquids*, 268 (2018) 315-325.
- [59] J. Zhao, X.J. Shen, X. Domene, J.M. Alcaniz, X. Liao, C. Palet, Comparison of biochars derived from different types of feedstock and their potential for heavy metal removal in multiple-metal solutions, *Sci Rep*, 9 (2019) 9869.

- [60] E. Agrafioti, D. Kalderis, E. Diamadopoulos, Arsenic and chromium removal from water using biochars derived from rice husk, organic solid wastes and sewage sludge, *J Environ Manage*, 133 (2014) 309-314.
- [61] S. Batool, M. Idrees, M.I. Al-Wabel, M. Ahmad, K. Hina, H. Ullah, L. Cui, Q. Hussain, Sorption of Cr(III) from aqueous media via naturally functionalized microporous biochar: Mechanistic study, *Microchemical Journal*, 144 (2019) 242-253.
- [62] M. Amin, P. Chetpattananondh, Biochar from extracted marine *Chlorella* sp. residue for high efficiency adsorption with ultrasonication to remove Cr(VI), Zn(II) and Ni(II), *Bioresour Technol*, 289 (2019) 121578.
- [63] Y. Li, Y. Wei, S. Huang, X. Liu, Z. Jin, M. Zhang, J. Qu, Y. Jin, Biosorption of Cr(VI) onto *Auricularia auricula* dreg biochar modified by cationic surfactant: Characteristics and mechanism, *Journal of Molecular Liquids*, 269 (2018) 824-832.
- [64] O.R. Harvey, B.E. Herbert, R.D. Rhue, L.J. Kuo, Metal interactions at the biochar-water interface: energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry, *Environ Sci Technol*, 45 (2011) 5550-5556.
- [65] T. Chen, Y. Zhang, H. Wang, W. Lu, Z. Zhou, Y. Zhang, L. Ren, Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge, *Bioresour Technol*, 164 (2014) 47-54.
- [66] A.R. Zimmerman, B. Gao, M.-Y. Ahn, Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils, *Soil Biology and Biochemistry*, 43 (2011) 1169-1179.
- [67] W. Suliman, J.B. Harsh, N.I. Abu-Lail, A.M. Fortuna, I. Dallmeyer, M. Garcia-Perez, Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties, *Biomass & Bioenergy*, 84 (2016) 37-48.
- [68] J. Xing, L. Li, G. Li, G. Xu, Feasibility of sludge-based biochar for soil remediation: Characteristics and safety performance of heavy metals influenced by pyrolysis temperatures, *Ecotoxicology and Environmental Safety*, 180 (2019) 457-465.
- [69] H. Nan, F. Yang, L. Zhao, O. Mašek, X. Cao, Z. Xiao, Interaction of Inherent Minerals with Carbon during Biomass Pyrolysis Weakens Biochar Carbon Sequestration Potential, *ACS Sustainable Chemistry & Engineering*, 7 (2019) 1591-1599.
- [70] L. Zhao, W. Zheng, X.D. Cao, Distribution and evolution of organic matter phases during biochar formation and their importance in carbon loss and pore structure, *Chemical Engineering Journal*, 250 (2014) 240-247.
- [71] K. Yoon, D.W. Cho, Y.F. Tsang, D.C.W. Tsang, E.E. Kwon, H. Song, Synthesis of functionalised biochar using red mud, lignin, and carbon dioxide as raw materials, *Chemical Engineering Journal*, 361 (2019) 1597-1604.
- [72] D.W. Cho, K. Yoon, Y. Ahn, Y. Sun, D.C.W. Tsang, D. Hou, Y.S. Ok, H. Song, Fabrication and environmental applications of multifunctional mixed metal-biochar composites (MMBC) from red mud and lignin wastes, *J Hazard Mater*, 374 (2019) 412-419.
- [73] Y. Yao, B. Gao, J. Chen, M. Zhang, M. Inyang, Y. Li, A. Alva, L. Yang, Engineered carbon (biochar) prepared by direct pyrolysis of Mg-accumulated tomato tissues: Characterization and phosphate removal potential, *Bioresour Technology*, 138 (2013) 8-13.
- [74] M. Chen, F. He, D. Hu, C. Bao, Q. Huang, Broadened operating pH range for adsorption/reduction of aqueous Cr(VI) using biochar from directly treated jute (*Corchorus capsularis* L.) fibers by H₃PO₄, *Chemical Engineering Journal*, 381 (2020) 122739.

- [75] R. Xiao, J.J. Wang, R. Li, J. Park, Y. Meng, B. Zhou, S. Pensky, Z. Zhang, Enhanced sorption of hexavalent chromium [Cr(VI)] from aqueous solutions by diluted sulfuric acid-assisted MgO-coated biochar composite, *Chemosphere*, 208 (2018) 408-416.
- [76] M.M. Mian, G. Liu, B. Yousaf, B. Fu, H. Ullah, M.U. Ali, Q. Abbas, M.A. Mujtaba Munir, L. Ruijia, Simultaneous functionalization and magnetization of biochar via NH₃ ambient pyrolysis for efficient removal of Cr (VI), *Chemosphere*, 208 (2018) 712-721.
- [77] Y. Xiao, H. Lyu, J. Tang, K. Wang, H. Sun, Effects of ball milling on the photochemistry of biochar: Enrofloxacin degradation and possible mechanisms, *Chemical Engineering Journal*, 384 (2020) 123311.
- [78] O. Mašek, V. Budarin, M. Gronnow, K. Crombie, P. Brownsort, E. Fitzpatrick, P. Hurst, Microwave and slow pyrolysis biochar—Comparison of physical and functional properties, *Journal of Analytical and Applied Pyrolysis*, 100 (2013) 41-48.
- [79] C. Guizani, M. Jeguirim, R. Gadiou, F.J. Escudero Sanz, S. Salvador, Biomass char gasification by H₂O, CO₂ and their mixture: Evolution of chemical, textural and structural properties of the chars, *Energy*, 112 (2016) 133-145.
- [80] B. Sajjadi, J.W. Broome, W.Y. Chen, D.L. Mattern, N.O. Egiebor, N. Hammer, C.L. Smith, Urea functionalization of ultrasound-treated biochar: A feasible strategy for enhancing heavy metal adsorption capacity, *Ultrasonics Sonochemistry*, 51 (2019) 20-30.
- [81] K. Wang, Y. Sun, J. Tang, J. He, H. Sun, Aqueous Cr(VI) removal by a novel ball milled Fe(0)-biochar composite: Role of biochar electron transfer capacity under high pyrolysis temperature, *Chemosphere*, 241 (2020) 125044.
- [82] T. Kan, V. Strezov, T.J. Evans, Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters, *Renewable and Sustainable Energy Reviews*, 57 (2016) 1126-1140.
- [83] S. Ramanayaka, D.C.W. Tsang, D. Hou, Y.S. Ok, M. Vithanage, Green synthesis of graphitic nanobiochar for the removal of emerging contaminants in aqueous media, *Science of The Total Environment*, 706 (2020) 135725.
- [84] Y. Wang, X.J. Wang, M. Liu, X. Wang, Z. Wu, L.Z. Yang, S.Q. Xia, J.F. Zhao, Cr(VI) removal from water using cobalt-coated bamboo charcoal prepared with microwave heating, *Industrial Crops and Products*, 39 (2012) 81-88.
- [85] X. Mao, Q.H. Kang, Y. Liu, A.A. Siyal, W.Y. Ao, C.M. Ran, J. Fu, Z.Y. Deng, Y.M. Song, J.J. Dai, Microwave-assisted pyrolysis of furfural residue in a continuously operated auger reactor: Biochar characterization and analysis, *Energy*, 168 (2019) 573-584.
- [86] D. Zhong, Y. Zhang, L. Wang, J. Chen, Y. Jiang, D.C.W. Tsang, Z. Zhao, S. Ren, Z. Liu, J.C. Crittenden, Mechanistic insights into adsorption and reduction of hexavalent chromium from water using magnetic biochar composite: Key roles of Fe₃O₄ and persistent free radicals, *Environ Pollut*, 243 (2018) 1302-1309.
- [87] A.U. Rajapaksha, M. Vithanage, M. Zhang, M. Ahmad, D. Mohan, S.X. Chang, Y.S. Ok, Pyrolysis condition affected sulfamethazine sorption by tea waste biochars, *Bioresource Technology*, 166 (2014) 303-308.
- [88] J. Lee, X. Yang, S.H. Cho, J.K. Kim, S.S. Lee, D.C.W. Tsang, Y.S. Ok, E.E. Kwon, Pyrolysis process of agricultural waste using CO₂ for waste management, energy recovery, and biochar fabrication, *Applied Energy*, 185 (2017) 214-222.
- [89] A.K. Biswas, K. Umeki, W. Yang, W. Blasiak, Change of pyrolysis characteristics and structure of woody biomass due to steam explosion pretreatment, *Fuel Processing Technology*, 92 (2011) 1849-

1854.

- [90] D. Feng, Y. Zhao, Y. Zhang, S. Sun, S. Meng, Y. Guo, Y. Huang, Effects of K and Ca on reforming of model tar compounds with pyrolysis biochars under H₂O or CO₂, *Chemical Engineering Journal*, 306 (2016) 422-432.
- [91] B. Chu, Y. Amano, M. Machida, Preparation of bean dreg derived N-doped activated carbon with high adsorption for Cr(VI), *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 586 (2020) 124262.
- [92] S. Banerjee, S. Barman, G. Halder, Elucidation of preferential elimination of Cr(VI) via bioinspired adsorbents: a comparative assessment, *Environmental Earth Sciences*, 78 (2019) 121.
- [93] R. Chatterjee, B. Sajjadi, D.L. Mattern, W.-Y. Chen, T. Zubatiuk, D. Leszczynska, J. Leszczynski, N.O. Egiebor, N. Hammer, Ultrasound cavitation intensified amine functionalization: A feasible strategy for enhancing CO₂ capture capacity of biochar, *Fuel*, 225 (2018) 287-298.
- [94] J. Yu, C. Jiang, Q. Guan, P. Ning, J. Gu, Q. Chen, J. Zhang, R. Miao, Enhanced removal of Cr(VI) from aqueous solution by supported ZnO nanoparticles on biochar derived from waste water hyacinth, *Chemosphere*, 195 (2018) 632-640.
- [95] L.L. Ling, W.J. Liu, S. Zhang, H. Jiang, Magnesium Oxide Embedded Nitrogen Self-Doped Biochar Composites: Fast and High-Efficiency Adsorption of Heavy Metals in an Aqueous Solution, *Environ Sci Technol*, 51 (2017) 10081-10089.
- [96] S. Zhang, H. Zhang, F. Liu, F. Yang, S. Zhou, K. Zheng, C. Chu, L. Liu, M. Ju, Effective removal of Cr(vi) from aqueous solution by biochar supported manganese sulfide, *Rsc Advances*, 9 (2019) 31333-31342.
- [97] M. Liang, S. Xu, Y. Zhu, X. Chen, Z. Deng, L. Yan, H. He, Preparation and Characterization of Fe-Mn Binary Oxide/Mulberry Stem Biochar Composite Adsorbent and Adsorption of Cr(VI) from Aqueous Solution, *International Journal of Environmental Research and Public Health*, 17 (2020).
- [98] D. Huang, C. Liu, C. Zhang, R. Deng, R. Wang, W. Xue, H. Luo, G. Zeng, Q. Zhang, X. Guo, Cr(VI) removal from aqueous solution using biochar modified with Mg/Al-layered double hydroxide intercalated with ethylenediaminetetraacetic acid, *Bioresource Technology*, 276 (2019) 127-132.
- [99] Y. Chen, B. Wang, J. Xin, P. Sun, D. Wu, Adsorption behavior and mechanism of Cr(VI) by modified biochar derived from *Enteromorpha prolifera*, *Ecotoxicol Environ Saf*, 164 (2018) 440-447.
- [100] B. Li, L. Yang, C.-q. Wang, Q.-p. Zhang, Q.-c. Liu, Y.-d. Li, R. Xiao, Adsorption of Cd(II) from aqueous solutions by rape straw biochar derived from different modification processes, *Chemosphere*, 175 (2017) 332-340.
- [101] H. Lyu, J. Tang, Y. Huang, L. Gai, E.Y. Zeng, K. Liber, Y. Gong, Removal of hexavalent chromium from aqueous solutions by a novel biochar supported nanoscale iron sulfide composite, *Chemical Engineering Journal*, 322 (2017) 516-524.
- [102] J. Shang, M. Zong, Y. Yu, X. Kong, Q. Du, Q. Liao, Removal of chromium (VI) from water using nanoscale zerovalent iron particles supported on herb-residue biochar, *Journal of Environmental Management*, 197 (2017) 331-337.
- [103] Y. Yang, K. Sun, L. Han, J. Jin, H. Sun, Y. Yang, B. Xing, Effect of minerals on the stability of biochar, *Chemosphere*, 204 (2018) 310-317.
- [104] S. Wang, B. Gao, Y. Li, A. Mosa, A.R. Zimmerman, L.Q. Ma, W.G. Harris, K.W. Migliaccio, Manganese oxide-modified biochars: preparation, characterization, and sorption of arsenate and lead, *Bioresour Technol*, 181 (2015) 13-17.
- [105] S. Wang, B. Gao, A.R. Zimmerman, Y. Li, L. Ma, W.G. Harris, K.W. Migliaccio, Removal of

arsenic by magnetic biochar prepared from pinewood and natural hematite, *Bioresource Technology*, 175 (2015) 391-395.

[106] F. Li, X. Cao, L. Zhao, J. Wang, Z. Ding, Effects of mineral additives on biochar formation: carbon retention, stability, and properties, *Environ Sci Technol*, 48 (2014) 11211-11217.

[107] A. Rawal, S.D. Joseph, J.M. Hook, C.H. Chia, P.R. Munroe, S. Donne, Y. Lin, D. Phelan, D.R.G. Mitchell, B. Pace, J. Horvat, J.B.W. Webber, Mineral–Biochar Composites: Molecular Structure and Porosity, *Environmental Science & Technology*, 50 (2016) 7706-7714.

[108] F. Xiao, J. Cheng, W. Cao, C. Yang, J. Chen, Z. Luo, Removal of heavy metals from aqueous solution using chitosan-combined magnetic biochars, *J Colloid Interface Sci*, 540 (2019) 579-584.

[109] S. Mandal, B. Sarkar, N. Bolan, Y.S. Ok, R. Naidu, Enhancement of chromate reduction in soils by surface modified biochar, *J Environ Manage*, 186 (2017) 277-284.

[110] X.F. Tan, Y.G. Liu, Y.L. Gu, Y. Xu, G.M. Zeng, X.J. Hu, S.B. Liu, X. Wang, S.M. Liu, J. Li, Biochar-based nano-composites for the decontamination of wastewater: A review, *Bioresour Technol*, 212 (2016) 318-333.

[111] M. Zhang, B. Gao, Y. Yao, Y. Xue, M. Inyang, Synthesis, characterization, and environmental implications of graphene-coated biochar, *Sci Total Environ*, 435-436 (2012) 567-572.

[112] A. Anstey, S. Vivekanandhan, A. Rodriguez-Urbe, M. Misra, A.K. Mohanty, Oxidative acid treatment and characterization of new biocarbon from sustainable Miscanthus biomass, *Science of The Total Environment*, 550 (2016) 241-247.

[113] Z. Ding, X. Hu, Y. Wan, S. Wang, B. Gao, Removal of lead, copper, cadmium, zinc, and nickel from aqueous solutions by alkali-modified biochar: Batch and column tests, *Journal of Industrial and Engineering Chemistry*, 33 (2016) 239-245.

[114] H. Peng, P. Gao, G. Chu, B. Pan, J. Peng, B. Xing, Enhanced adsorption of Cu (II) and Cd (II) by phosphoric acid-modified biochars, *Environmental Pollution*, 229 (2017) 846-853.

[115] N. Zhao, C. Zhao, Y. Lv, W. Zhang, Y. Du, Z. Hao, J. Zhang, Adsorption and coadsorption mechanisms of Cr(VI) and organic contaminants on H₃PO₄ treated biochar, *Chemosphere*, 186 (2017) 422-429.

[116] L. Lonappan, Y. Liu, T. Rouissi, S.K. Brar, R.Y. Surampalli, Development of biochar-based green functional materials using organic acids for environmental applications, *Journal of Cleaner Production*, 244 (2020) 118841.

[117] S. Zhu, X. Huang, X. Yang, P. Peng, Z. Li, C. Jin, Enhanced Transformation of Cr(VI) by Heterocyclic-N within Nitrogen-Doped Biochar: Impact of Surface Modulatory Persistent Free Radicals (PFRs), *Environmental Science & Technology*, 54 (2020) 8123-8132.

[118] Q. Chai, L. Lu, Y. Lin, X. Ji, C. Yang, S. He, D. Zhang, Effects and mechanisms of anionic and nonionic surfactants on biochar removal of chromium, *Environ Sci Pollut Res Int*, 25 (2018) 18443-18450.

[119] C. Wan, Y. Li, Fungal pretreatment of lignocellulosic biomass, *Biotechnol Adv*, 30 (2012) 1447-1457.

[120] M. Inyang, B. Gao, P. Pullammanappallil, W. Ding, A.R. Zimmerman, Biochar from anaerobically digested sugarcane bagasse, *Bioresource Technology*, 101 (2010) 8868-8872.

[121] W. Zhang, H. Cheng, Q. Niu, M. Fu, H. Huang, D. Ye, Microbial Targeted Degradation Pretreatment: A Novel Approach to Preparation of Activated Carbon with Specific Hierarchical Porous Structures, High Surface Areas, and Satisfactory Toluene Adsorption Performance, *Environ Sci Technol*, 53 (2019) 7632-7640.

- [122] K. Zhang, M. Liu, T. Zhang, X. Min, Z. Wang, L. Chai, Y. Shi, High-performance supercapacitor energy storage using a carbon material derived from lignin by bacterial activation before carbonization, *J Mater Chem A*, 7 (2019) 26838-26848.
- [123] L. Hale, M. Luth, D. Crowley, Biochar characteristics relate to its utility as an alternative soil inoculum carrier to peat and vermiculite, *Soil Biology & Biochemistry*, 81 (2015) 228-235.
- [124] S. Shi, J. Yang, S. Liang, M. Li, Q. Gan, K. Xiao, J. Hu, Enhanced Cr(VI) removal from acidic solutions using biochar modified by $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ particles, *Science of The Total Environment*, 628-629 (2018) 499-508.
- [125] X. Wang, J. Xu, J. Liu, J. Liu, F. Xia, C. Wang, R.A. Dahlgren, W. Liu, Mechanism of Cr(VI) removal by magnetic greigite/biochar composites, *Science of The Total Environment*, 700 (2020) 134414.
- [126] N. Zhao, Z. Yin, F. Liu, M. Zhang, Y. Lv, Z. Hao, G. Pan, J. Zhang, Environmentally persistent free radicals mediated removal of Cr(VI) from highly saline water by corn straw biochars, *Bioresour Technol*, 260 (2018) 294-301.
- [127] Z. Xu, X. Xu, X. Tao, C. Yao, D.C.W. Tsang, X. Cao, Interaction with low molecular weight organic acids affects the electron shuttling of biochar for Cr(VI) reduction, *Journal of Hazardous Materials*, 378 (2019) 120705.
- [128] K. Li, Z. Huang, S. Zhu, S. Luo, L. Yan, Y. Dai, Y. Guo, Y. Yang, Removal of Cr(VI) from water by a biochar-coupled g- C_3N_4 nanosheets composite and performance of a recycled photocatalyst in single and combined pollution systems, *Applied Catalysis B: Environmental*, 243 (2019) 386-396.
- [129] P. Jeon, M.-E. Lee, K. Baek, Adsorption and photocatalytic activity of biochar with graphitic carbon nitride (g- C_3N_4), *Journal of the Taiwan Institute of Chemical Engineers*, 77 (2017) 244-249.
- [130] E.S. Odinga, M.G. Waigi, F.O. Gudda, J. Wang, B. Yang, X. Hu, S. Li, Y. Gao, Occurrence, formation, environmental fate and risks of environmentally persistent free radicals in biochars, *Environment International*, 134 (2020) 105172.
- [131] W. Zhu, D. Yu, M. Shi, Y. Zhang, T. Huang, Quinone-Mediated Microbial Goethite Reduction and Transformation of Redox Mediator, Anthraquinone-2,6-Disulfonate (AQDS), *Geomicrobiology Journal*, 34 (2016) 27-36.
- [132] J. Yang, B. Pan, H. Li, S. Liao, D. Zhang, M. Wu, B. Xing, Degradation of p-Nitrophenol on Biochars: Role of Persistent Free Radicals, *Environ Sci Technol*, 50 (2016) 694-700.
- [133] G. Fang, C. Liu, J. Gao, D.D. Dionysiou, D. Zhou, Manipulation of persistent free radicals in biochar to activate persulfate for contaminant degradation, *Environ Sci Technol*, 49 (2015) 5645-5653.
- [134] Y. Xu, Z. Lou, P. Yi, J. Chen, X. Ma, Y. Wang, M. Li, W. Chen, Q. Liu, J. Zhou, J. Zhang, G. Qian, Improving abiotic reducing ability of hydrothermal biochar by low temperature oxidation under air, *Bioresource Technology*, 172 (2014) 212-218.
- [135] X. Ruan, Y. Liu, G. Wang, R.L. Frost, G. Qian, D.C.W. Tsang, Transformation of functional groups and environmentally persistent free radicals in hydrothermal carbonisation of lignin, *Bioresource Technology*, 270 (2018) 223-229.
- [136] K. Zhang, P. Sun, M.C.A.S. Faye, Y. Zhang, Characterization of biochar derived from rice husks and its potential in chlorobenzene degradation, *Carbon*, 130 (2018) 730-740.
- [137] A.T. Tag, G. Duman, S. Ucar, J. Yanik, Effects of feedstock type and pyrolysis temperature on potential applications of biochar, *Journal of Analytical and Applied Pyrolysis*, 120 (2016) 200-206.
- [138] K.B. Cantrell, P.G. Hunt, M. Uchimiya, J.M. Novak, K.S. Ro, Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar, *Bioresource Technology*, 107 (2012)

419-428.

- [139] S. Chen, A.E. Rotaru, P.M. Shrestha, N.S. Malvankar, F. Liu, W. Fan, K.P. Nevin, D.R. Lovley, Promoting interspecies electron transfer with biochar, *Sci Rep*, 4 (2014) 5019.
- [140] P. Zhang, S. Zheng, J. Liu, B. Wang, F. Liu, Y. Feng, Surface properties of activated sludge-derived biochar determine the facilitating effects on *Geobacter* co-cultures, *Water Research*, 142 (2018) 441-451.
- [141] L. Klupfel, M. Keiluweit, M. Kleber, M. Sander, Redox properties of plant biomass-derived black carbon (biochar), *Environ Sci Technol*, 48 (2014) 5601-5611.
- [142] M. Zhou, C. Zhang, Y. Yuan, X. Mao, Y. Li, N. Wang, S. Wang, X. Wang, Pinewood outperformed bamboo as feedstock to prepare biochar-supported zero-valent iron for Cr⁶⁺ reduction, *Environmental Research*, 187 (2020) 109695.
- [143] J. Ai, H. Ma, D.J. Tobler, M.C. Mangayayam, C. Lu, F.W.J. van den Berg, W. Yin, H.C. Bruun Hansen, Bone Char Mediated Dechlorination of Trichloroethylene by Green Rust, *Environmental Science & Technology*, 54 (2020) 3643-3652.
- [144] G. Wang, Q. Li, Y. Li, Y. Xing, G. Yao, Y. Liu, R. Chen, X.C. Wang, Redox-active biochar facilitates potential electron transfer between syntrophic partners to enhance anaerobic digestion under high organic loading rate, *Bioresource Technology*, 298 (2020) 122524.
- [145] B. Zhang, S. Zhou, L. Zhou, J. Wen, Y. Yuan, Pyrolysis temperature-dependent electron transfer capacities of dissolved organic matters derived from wheat straw biochar, *Science of The Total Environment*, 696 (2019) 133895.
- [146] A. Prevotau, F. Ronsse, I. Cid, P. Boeckx, K. Rabaey, The electron donating capacity of biochar is dramatically underestimated, *Sci Rep*, 6 (2016) 32870.
- [147] T. Sun, B.D.A. Levin, M.P. Schmidt, J.J.L. Guzman, A. Enders, C.E. Martinez, D.A. Muller, L.T. Angenent, J. Lehmann, Simultaneous Quantification of Electron Transfer by Carbon Matrices and Functional Groups in Pyrogenic Carbon, *Environ Sci Technol*, 52 (2018) 8538-8547.
- [148] G. Fang, C. Liu, Y. Wang, D.D. Dionysiou, D. Zhou, Photogeneration of reactive oxygen species from biochar suspension for diethyl phthalate degradation, *Applied Catalysis B-Environmental*, 214 (2017) 34-45.
- [149] N. Chen, Y. Huang, X. Hou, Z. Ai, L. Zhang, Photochemistry of Hydrochar: Reactive Oxygen Species Generation and Sulfadimidine Degradation, *Environ Sci Technol*, 51 (2017) 11278-11287.
- [150] R. Li, D. Hu, K. Hu, H. Deng, M. Zhang, A. Wang, R. Qiu, K. Yan, Coupling adsorption-photocatalytic reduction of Cr(VI) by metal-free N-doped carbon, *Science of The Total Environment*, 704 (2020) 135284.
- [151] H.-B. Kim, J.-G. Kim, J.-H. Choi, E.E. Kwon, K. Baek, Photo-induced redox coupling of dissolved organic matter and iron in biochars and soil system: Enhanced mobility of arsenic, *Science of The Total Environment*, 689 (2019) 1037-1043.
- [152] Y. Tian, L. Feng, C. Wang, Y. Liu, J. Zou, R. Li, Z. Du, L. Zhang, Dissolved black carbon enhanced the aquatic photo-transformation of chlortetracycline via triplet excited-state species: The role of chemical composition, *Environ Res*, 179 (2019) 108855.
- [153] H.B. Kim, J.G. Kim, S.H. Kim, E.E. Kwon, K. Baek, Consecutive reduction of Cr(VI) by Fe(II) formed through photo-reaction of iron-dissolved organic matter originated from biochar, *Environ Pollut*, 253 (2019) 231-238.
- [154] H. Fu, H. Liu, J. Mao, W. Chu, Q. Li, P.J.J. Alvarez, X. Qu, D. Zhu, Photochemistry of Dissolved Black Carbon Released from Biochar: Reactive Oxygen Species Generation and Phototransformation,

- Environmental Science & Technology, 50 (2016) 1218-1226.
- [155] L. Zhou, Y. Liu, S. Liu, Y. Yin, G. Zeng, X. Tan, X. Hu, X. Hu, L. Jiang, Y. Ding, S. Liu, X. Huang, Investigation of the adsorption-reduction mechanisms of hexavalent chromium by ramie biochars of different pyrolytic temperatures, *Bioresour Technol*, 218 (2016) 351-359.
- [156] X. Dong, L.Q. Ma, Y. Li, Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing, *Journal of Hazardous Materials*, 190 (2011) 909-915.
- [157] Z. Xu, X. Xu, Y. Zhang, Y. Yu, X. Cao, Pyrolysis-temperature depended electron donating and mediating mechanisms of biochar for Cr(VI) reduction, *Journal of Hazardous Materials*, 388 (2019) 121794.
- [158] Y. Zhu, H. Li, G. Zhang, F. Meng, L. Li, S. Wu, Removal of hexavalent chromium from aqueous solution by different surface-modified biochars: Acid washing, nanoscale zero-valent iron and ferric iron loading, *Bioresour Technol*, 261 (2018) 142-150.
- [159] T.M. Abdel-Fattah, M.E. Mahmoud, S.B. Ahmed, M.D. Huff, J.W. Lee, S. Kumar, Biochar from woody biomass for removing metal contaminants and carbon sequestration, *Journal of Industrial and Engineering Chemistry*, 22 (2015) 103-109.
- [160] Y.P. Zhang, V.S.K. Adi, H.L. Huang, H.P. Lin, Z.H. Huang, Adsorption of metal ions with biochars derived from biomass wastes in a fixed column: Adsorption isotherm and process simulation, *Journal of Industrial and Engineering Chemistry*, 76 (2019) 240-244.
- [161] Y. Liu, S.P. Sohi, S. Liu, J. Guan, J. Zhou, J. Chen, Adsorption and reductive degradation of Cr(VI) and TCE by a simply synthesized zero valent iron magnetic biochar, *J Environ Manage*, 235 (2019) 276-281.
- [162] M. Teixido, C. Hurtado, J.J. Pignatello, J.L. Beltran, M. Granados, J. Peccia, Predicting contaminant adsorption in black carbon (biochar)-amended soil for the veterinary antimicrobial sulfamethazine, *Environ Sci Technol*, 47 (2013) 6197-6205.
- [163] S.M. Shaheen, N.K. Niazi, N.E.E. Hassan, I. Bibi, H. Wang, Daniel C.W. Tsang, Y.S. Ok, N. Bolan, J. Rinklebe, Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review, *International Materials Reviews*, 64 (2019) 216-247.
- [164] X. Xu, H. Huang, Y. Zhang, Z. Xu, X. Cao, Biochar as both electron donor and electron shuttle for the reduction transformation of Cr(VI) during its sorption, *Environ Pollut*, 244 (2019) 423-430.
- [165] A.D. Igalavithana, S. Mandal, N.K. Niazi, M. Vithanage, S.J. Parikh, F.N.D. Mukome, M. Rizwan, P. Oleszczuk, M. Al-Wabel, N. Bolan, D.C.W. Tsang, K.-H. Kim, Y.S. Ok, Advances and future directions of biochar characterization methods and applications, *Critical Reviews in Environmental Science and Technology*, 47 (2017) 2275-2330.
- [166] T. Chen, Z. Zhou, S. Xu, H. Wang, W. Lu, Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge, *Bioresource Technology*, 190 (2015) 388-394.
- [167] Z.-h. Yang, S. Xiong, B. Wang, Q. Li, W.-c. Yang, Cr(III) adsorption by sugarcane pulp residue and biochar, *Journal of Central South University*, 20 (2013) 1319-1325.
- [168] J. Pan, J. Jiang, R. Xu, Adsorption of Cr(III) from acidic solutions by crop straw derived biochars, *Journal of Environmental Sciences*, 25 (2013) 1957-1965.
- [169] Y. Han, X. Cao, X. Ouyang, S.P. Sohi, J. Chen, Adsorption kinetics of magnetic biochar derived from peanut hull on removal of Cr (VI) from aqueous solution: Effects of production conditions and particle size, *Chemosphere*, 145 (2016) 336-341.
- [170] W. Wang, B. Hu, C. Wang, Z. Liang, F. Cui, Z. Zhao, C. Yang, Cr(VI) removal by micron-scale

iron-carbon composite induced by ball milling: The role of activated carbon, *Chemical Engineering Journal*, 389 (2020).

[171] S. Banerjee, S. Barman, G. Halder, Elucidation of preferential elimination of Cr(VI) via bioinspired adsorbents: a comparative assessment, *Environmental Earth Sciences*, 78 (2019).

[172] L. Long, Y. Xue, X. Hu, Y. Zhu, Study on the influence of surface potential on the nitrate adsorption capacity of metal modified biochar, *Environmental Science and Pollution Research*, 26 (2019) 3065-3074.

[173] Y. Ma, W.J. Liu, N. Zhang, Y.S. Li, H. Jiang, G.P. Sheng, Polyethylenimine modified biochar adsorbent for hexavalent chromium removal from the aqueous solution, *Bioresour Technol*, 169 (2014) 403-408.

[174] J. Mokrzycki, I. Michalak, P. Rutkowski, Tomato green waste biochars as sustainable trivalent chromium sorbents, *Environmental Science and Pollution Research*, (2019).

[175] C.A. Masiello, Y. Chen, X. Gao, S. Liu, H.Y. Cheng, M.R. Bennett, J.A. Rudgers, D.S. Wagner, K. Zygourakis, J.J. Silberg, Biochar and microbial signaling: production conditions determine effects on microbial communication, *Environ Sci Technol*, 47 (2013) 11496-11503.

[176] R.A. Hill, J. Hunt, E. Sanders, M. Tran, G.A. Burk, T.E. Mlsna, N.C. Fitzkee, Effect of Biochar on Microbial Growth: A Metabolomics and Bacteriological Investigation in *E. coli*, *Environ Sci Technol*, 53 (2019) 2635-2646.

[177] L. Chai, C. Ding, J. Li, Z. Yang, Y. Shi, Multi-omics response of *Pannonibacter phragmitetus* BB to hexavalent chromium, *Environmental Pollution*, 249 (2019) 63-73.

[178] T.U. Han, J. Kim, K. Kim, Freezing-accelerated removal of chromate by biochar synthesized from waste rice husk, *Separation and Purification Technology*, 250 (2020) 117233.

[179] C.-H. Liu, W. Chu, H. Li, S.A. Boyd, B.J. Teppen, J. Mao, J. Lehmann, W. Zhang, Quantification and characterization of dissolved organic carbon from biochars, *Geoderma*, 335 (2019) 161-169.

[180] X. Zheng, Y. Liu, H. Fu, X. Qu, M. Yan, S. Zhang, D. Zhu, Comparing electron donating/accepting capacities (EDC/EAC) between crop residue-derived dissolved black carbon and standard humic substances, *Science of The Total Environment*, 673 (2019) 29-35.

[181] M. Aeschbacher, C. Graf, R.P. Schwarzenbach, M. Sander, Antioxidant Properties of Humic Substances, *Environmental Science & Technology*, 46 (2012) 4916-4925.

[182] Y. Zhang, N. Liu, Y. Yang, J. Li, S. Wang, J. Lv, R. Tang, Novel carbothermal synthesis of Fe, N co-doped oak wood biochar (Fe/N-OB) for fast and effective Cr(VI) removal, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 600 (2020) 124926.

[183] J. Xu, Y. Dai, Y. Shi, S. Zhao, H. Tian, K. Zhu, H. Jia, Mechanism of Cr(VI) reduction by humin: Role of environmentally persistent free radicals and reactive oxygen species, *Science of The Total Environment*, 725 (2020) 138413.

[184] K. Zhang, P. Sun, Y. Zhang, Decontamination of Cr(VI) facilitated formation of persistent free radicals on rice husk derived biochar, *Frontiers of Environmental Science & Engineering*, 13 (2019).

[185] Q. Shao, C. Xu, Y. Wang, S. Huang, B. Zhang, L. Huang, D. Fan, P.G. Tratnyek, Dynamic interactions between sulfidated zerovalent iron and dissolved oxygen: Mechanistic insights for enhanced chromate removal, *Water Res*, 135 (2018) 322-330.

[186] L. Liu, X. Liu, D. Wang, H. Lin, L. Huang, Removal and reduction of Cr(VI) in simulated wastewater using magnetic biochar prepared by co-pyrolysis of nano-zero-valent iron and sewage sludge, *Journal of Cleaner Production*, 257 (2020) 120562.

[187] E.R. Graber, L. Tsechansky, B. Lew, E. Cohen, Reducing capacity of water extracts of biochars

- and their solubilization of soil Mn and Fe, *European Journal of Soil Science*, 65 (2014) 162-172.
- [188] S. Zhu, X. Huang, D. Wang, L. Wang, F. Ma, Enhanced hexavalent chromium removal performance and stabilization by magnetic iron nanoparticles assisted biochar in aqueous solution: Mechanisms and application potential, *Chemosphere*, 207 (2018) 50-59.
- [189] D.A. Brose, B.R. James, Oxidation-Reduction Transformations of Chromium in Aerobic Soils and the Role of Electron-Shuttling Quinones, *Environmental Science & Technology*, 44 (2010) 9438-9444.
- [190] A. Kappler, M.L. Wuestner, A. Ruecker, J. Harter, M. Halama, S. Behrens, Biochar as an Electron Shuttle between Bacteria and Fe(III) Minerals, *Environmental Science & Technology Letters*, 1 (2014) 339-344.
- [191] J.M. Byrne, N. Klueglein, C. Pearce, K.M. Rosso, E. Appel, A. Kappler, Redox cycling of Fe(II) and Fe(III) in magnetite by Fe-metabolizing bacteria, *Science*, 347 (2015) 1473-1476.
- [192] T. Sun, B.D. Levin, J.J. Guzman, A. Enders, D.A. Muller, L.T. Angenent, J. Lehmann, Rapid electron transfer by the carbon matrix in natural pyrogenic carbon, *Nat Commun*, 8 (2017) 14873.
- [193] J. Qin, Q. Li, Y. Liu, A. Niu, C. Lin, Biochar-driven reduction of As(V) and Cr(VI): Effects of pyrolysis temperature and low-molecular-weight organic acids, *Ecotoxicology and Environmental Safety*, 201 (2020) 110873.
- [194] J.M. Saquing, Y.-H. Yu, P.C. Chiu, Wood-Derived Black Carbon (Biochar) as a Microbial Electron Donor and Acceptor, *Environmental Science & Technology Letters*, 3 (2016) 62-66.
- [195] H.B. Gray, J.R. Winkler, Long-range electron transfer, *P Natl Acad Sci USA*, 102 (2005) 3534-3539.
- [196] G. Fang, J. Gao, C. Liu, D.D. Dionysiou, Y. Wang, D. Zhou, Key role of persistent free radicals in hydrogen peroxide activation by biochar: implications to organic contaminant degradation, *Environ Sci Technol*, 48 (2014) 1902-1910.
- [197] J. Han, M. Wang, G. Zhang, F. Zhan, D. Cai, Z. Wu, Probing the Migration of Free Radicals in Solid and Liquid Media via Cr(VI) Reduction by High-Energy Electron Beam Irradiation, *Scientific Reports*, 8 (2018) 15196.
- [198] H. Peng, J. Guo, Z. Liu, C. Tao, Direct advanced oxidation process for chromium(III) with sulfate free radicals, *SN Applied Sciences*, 1 (2018) 14.
- [199] Z. Yang, A. Kappler, J. Jiang, Reducing Capacities and Distribution of Redox-Active Functional Groups in Low Molecular Weight Fractions of Humic Acids, *Environmental Science & Technology*, 50 (2016) 12105-12113.
- [200] W.J. Liu, L.L. Ling, Y.Y. Wang, H. He, Y.R. He, H.Q. Yu, H. Jiang, One-pot high yield synthesis of Ag nanoparticle-embedded biochar hybrid materials from waste biomass for catalytic Cr(VI) reduction, *Environmental Science-Nano*, 3 (2016) 745-753.
- [201] R. Jia, Z. Qu, P. You, D. Qu, Effect of biochar on photosynthetic microorganism growth and iron cycling in paddy soil under different phosphate levels, *Science of the Total Environment*, 612 (2018) 223-230.
- [202] S. Xu, D. Adhikari, R. Huang, H. Zhang, Y. Tang, E. Roden, Y. Yang, Biochar-Facilitated Microbial Reduction of Hematite, *Environ Sci Technol*, 50 (2016) 2389-2395.
- [203] C. Wu, W. An, Z. Liu, J. Lin, Z. Qian, S. Xue, The effects of biochar as the electron shuttle on the ferrihydrite reduction and related arsenic (As) fate, *J Hazard Mater*, (2019) 121391.
- [204] X.N. Huang, D. Min, D.F. Liu, L. Cheng, C. Qian, W.W. Li, H.Q. Yu, Formation mechanism of organo-chromium (III) complexes from bioreduction of chromium (VI) by *Aeromonas hydrophila*,

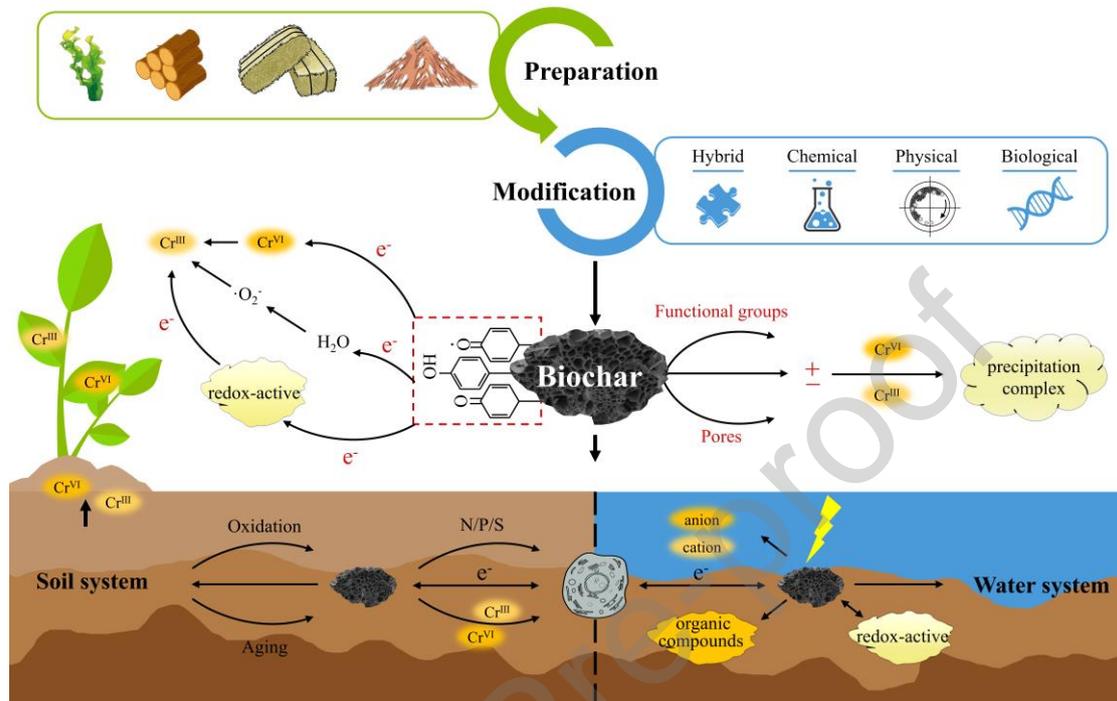
Environ Int, 129 (2019) 86-94.

- [205] S. Zhou, B. Zhang, Z. Liao, L. Zhou, Y. Yuan, Autochthonous N-doped carbon nanotube/activated carbon composites derived from industrial paper sludge for chromate (VI) reduction in microbial fuel cells, *Science of The Total Environment*, 712 (2020) 136513.
- [206] S.F. Jiang, L.L. Ling, Z.R. Xu, W.J. Liu, H. Jiang, Enhancing the Catalytic Activity and Stability of Noble Metal Nanoparticles by the Strong Interaction of Magnetic Biochar Support, *Industrial & Engineering Chemistry Research*, 57 (2018) 13055-13064.
- [207] T. Wang, S. Liu, W. Mao, Y. Bai, K. Chiang, K. Shah, J. Paz-Ferreiro, Novel Bi₂WO₆ loaded N-biochar composites with enhanced photocatalytic degradation of rhodamine B and Cr(VI), *Journal of Hazardous Materials*, 389 (2020) 121827.
- [208] S.F. Jiang, K.F. Xi, J. Yang, H. Jiang, Biochar-supported magnetic noble metallic nanoparticles for the fast recovery of excessive reductant during pollutant reduction, *Chemosphere*, 227 (2019) 63-71.
- [209] X. Shen, T. Zheng, J. Yang, Z. Shi, Q. Xue, W. Liu, S. Shan, M.H. Wong, Removal of Cr(VI) from Acid Wastewater by BC/ZnFe₂O₄ Magnetic Nanocomposite via the Synergy of Adsorption-Photocatalysis, *ChemCatChem*, 12 (2020) 4121-4131.
- [210] T. Yang, L. Meng, S. Han, J. Hou, S. Wang, X. Wang, Simultaneous reductive and sorptive removal of Cr(vi) by activated carbon supported β-FeOOH, *RSC Advances*, 7 (2017) 34687-34693.
- [211] Y. Qiu, Q. Zhang, B. Gao, M. Li, Z. Fan, W. Sang, H. Hao, X. Wei, Removal mechanisms of Cr(VI) and Cr(III) by biochar supported nanosized zero-valent iron: Synergy of adsorption, reduction and transformation, *Environmental Pollution*, 265 (2020) 115018.
- [212] H. Wang, S. Wang, Z. Chen, X. Zhou, J. Wang, Z. Chen, Engineered biochar with anisotropic layered double hydroxide nanosheets to simultaneously and efficiently capture Pb²⁺ and CrO₄²⁻ from electroplating wastewater, *Bioresource Technology*, 306 (2020) 123118.
- [213] P. Vassileva, A. Detcheva, I. Uzunov, S. Uzunova, Removal of Metal Ions from Aqueous Solutions Using Pyrolyzed Rice Husks: Adsorption Kinetics and Equilibria, *Chemical Engineering Communications*, 200 (2013) 1578-1599.
- [214] K. Zhang, A. Khan, P. Sun, Y. Zhang, A. Taraqqi-A-Kamal, Y. Zhang, Simultaneous reduction of Cr(VI) and oxidization of organic pollutants by rice husk derived biochar and the interactive influences of coexisting Cr(VI), *Science of The Total Environment*, 706 (2020) 135763.
- [215] W. Zhang, J. Zheng, P. Zheng, R. Qiu, Atrazine immobilization on sludge derived biochar and the interactive influence of coexisting Pb(II) or Cr(VI) ions, *Chemosphere*, 134 (2015) 438-445.
- [216] M.I. Bautista-Toledo, J. Rivera-Utrilla, R. Ocampo-Pérez, F. Carrasco-Marín, M. Sánchez-Polo, Cooperative adsorption of bisphenol-A and chromium(III) ions from water on activated carbons prepared from olive-mill waste, *Carbon*, 73 (2014) 338-350.
- [217] G. Darmograi, B. PreLOT, A. Geneste, G. Martin-Gassin, F. Salles, J. Zajac, How Does Competition between Anionic Pollutants Affect Adsorption onto Mg-Al Layered Double Hydroxide? Three Competition Schemes, *Journal of Physical Chemistry C*, 120 (2016) 10410-10418.
- [218] D. Dias, M. Bernardo, I. Matos, I. Fonseca, F. Pinto, N. Lapa, Activation of co-pyrolysis chars from rice wastes to improve the removal of Cr³⁺ from simulated and real industrial wastewaters, *Journal of Cleaner Production*, 267 (2020) 121993.
- [219] A. Cross, S.P. Sohi, The priming potential of biochar products in relation to labile carbon contents and soil organic matter status, *Soil Biology and Biochemistry*, 43 (2011) 2127-2134.
- [220] J. Lehmann, M.C. Rillig, J. Thies, C.A. Masiello, W.C. Hockaday, D. Crowley, Biochar effects on

- soil biota – A review, *Soil Biology and Biochemistry*, 43 (2011) 1812-1836.
- [221] S. Khan, C. Chao, M. Waqas, H.P. Arp, Y.G. Zhu, Sewage sludge biochar influence upon rice (*Oryza sativa* L) yield, metal bioaccumulation and greenhouse gas emissions from acidic paddy soil, *Environ Sci Technol*, 47 (2013) 8624-8632.
- [222] S. Gul, J.K. Whalen, B.W. Thomas, V. Sachdeva, H.Y. Deng, Physico-chemical properties and microbial responses in biochar-amended soils: Mechanisms and future directions, *Agriculture Ecosystems & Environment*, 206 (2015) 46-59.
- [223] M.A. Bashir, M. Naveed, M. Khalid, R. Ahmad, B. Gao, Influence of feedstock and pyrolytic temperature of biochar on physico-chemical characteristics and sorption of chromium in tannery polluted soil, *International Journal of Agriculture and Biology*, (2018).
- [224] S. Bashir, Q. Hussain, M. Akmal, M. Riaz, H. Hu, S.S. Ijaz, M. Iqbal, S. Abro, S. Mehmood, M. Ahmad, Sugarcane bagasse-derived biochar reduces the cadmium and chromium bioavailability to mash bean and enhances the microbial activity in contaminated soil, *Journal of Soils and Sediments*, 18 (2018) 874-886.
- [225] A.Z. Khan, S. Khan, T. Ayaz, M.L. Brusseau, M.A. Khan, J. Nawab, S. Muhammad, Popular wood and sugarcane bagasse biochars reduced uptake of chromium and lead by lettuce from mine-contaminated soil, *Environmental Pollution*, 263 (2020) 114446.
- [226] X. Liu, L. Yang, H. Zhao, W. Wang, Pyrolytic production of zerovalent iron nanoparticles supported on rice husk-derived biochar: simple, in situ synthesis and use for remediation of Cr(VI)-polluted soils, *Science of The Total Environment*, 708 (2020) 134479.
- [227] H. Su, Z. Fang, P.E. Tsang, J. Fang, D. Zhao, Stabilisation of nanoscale zero-valent iron with biochar for enhanced transport and in-situ remediation of hexavalent chromium in soil, *Environmental Pollution*, 214 (2016) 94-100.
- [228] N. Hemati Matin, M. Jalali, W. Buss, Synergistic immobilization of potentially toxic elements (PTEs) by biochar and nanoparticles in alkaline soil, *Chemosphere*, 241 (2020) 124932.
- [229] J. Chen, X. Liu, J. Zheng, B. Zhang, H. Lu, Z. Chi, G. Pan, L. Li, J. Zheng, X. Zhang, J. Wang, X. Yu, Biochar soil amendment increased bacterial but decreased fungal gene abundance with shifts in community structure in a slightly acid rice paddy from Southwest China, *Applied Soil Ecology*, 71 (2013) 33-44.
- [230] R.S. Quilliam, H.C. Glanville, S.C. Wade, D.L. Jones, Life in the 'charosphere' – Does biochar in agricultural soil provide a significant habitat for microorganisms?, *Soil Biology and Biochemistry*, 65 (2013) 287-293.
- [231] H. Lyu, H. Zhao, J. Tang, Y. Gong, Y. Huang, Q. Wu, B. Gao, Immobilization of hexavalent chromium in contaminated soils using biochar supported nanoscale iron sulfide composite, *Chemosphere*, 194 (2018) 360-369.
- [232] M. Arshad, A.H.A. Khan, I. Hussain, Z. Badar uz, M. Anees, M. Iqbal, G. Soja, C. Linde, S. Yousaf, The reduction of chromium (VI) phytotoxicity and phytoavailability to wheat (*Triticum aestivum* L.) using biochar and bacteria, *Applied Soil Ecology*, 114 (2017) 90-98.
- [233] J. Nawab, J. Ghani, S. Khan, W. Xiaoping, Minimizing the risk to human health due to the ingestion of arsenic and toxic metals in vegetables by the application of biochar, farmyard manure and peat moss, *J Environ Manage*, 214 (2018) 172-183.
- [234] H. Sarma, S. Sonowal, M.N.V. Prasad, Plant-microbiome assisted and biochar-amended remediation of heavy metals and polyaromatic compounds horizontal line a microcosmic study, *Ecotoxicol Environ Saf*, 176 (2019) 288-299.

- [235] M.A. Bashir, M. Naveed, Z. Ahmad, B. Gao, A. Mustafa, A. Núñez-Delgado, Combined application of biochar and sulfur regulated growth, physiological, antioxidant responses and Cr removal capacity of maize (*Zea mays* L.) in tannery polluted soils, *Journal of Environmental Management*, 259 (2020) 110051.
- [236] L. Abou Jaoude, P. Castaldi, N. Nassif, M.V. Pinna, G. Garau, Biochar and compost as gentle remediation options for the recovery of trace elements-contaminated soils, *The Science of the total environment*, 711 (2020) 134511-134511.
- [237] E. He, Y. Yang, Z. Xu, H. Qiu, F. Yang, W.J.G.M. Peijnenburg, W. Zhang, R. Qiu, S. Wang, Two years of aging influences the distribution and lability of metal(loid)s in a contaminated soil amended with different biochars, *Science of The Total Environment*, 673 (2019) 245-253.
- [238] M.V. Rechberger, S. Kloss, H. Rennhofer, J. Tintner, A. Watzinger, G. Soja, H. Lichtenegger, F. Zehetner, Changes in biochar physical and chemical properties: Accelerated biochar aging in an acidic soil, *Carbon*, 115 (2017) 209-219.
- [239] H. Wang, M. Feng, F. Zhou, X. Huang, D.C.W. Tsang, W. Zhang, Effects of atmospheric ageing under different temperatures on surface properties of sludge-derived biochar and metal/metalloid stabilization, *Chemosphere*, 184 (2017) 176-184.
- [240] Y. Lin, P. Munroe, S. Joseph, S. Kimber, L. Van Zwieten, Nanoscale organo-mineral reactions of biochar in ferrosol: an investigation using microscopy, *Plant and Soil*, 357 (2012) 369-380.
- [241] F. Yang, L. Zhao, B. Gao, X. Xu, X. Cao, The Interfacial Behavior between Biochar and Soil Minerals and Its Effect on Biochar Stability, *Environmental Science & Technology*, 50 (2016) 2264-2271.
- [242] X. Ren, F. Wang, P. Zhang, J. Guo, H. Sun, Aging effect of minerals on biochar properties and sorption capacities for atrazine and phenanthrene, *Chemosphere*, 206 (2018) 51-58.
- [243] Z. Xu, X. Xu, D.C.W. Tsang, F. Yang, L. Zhao, H. Qiu, X. Cao, Participation of soil active components in the reduction of Cr(VI) by biochar: Differing effects of iron mineral alone and its combination with organic acid, *Journal of hazardous materials*, 384 (2020) 121455-121455.

Graphical abstract



Highlights

- Hybrid and biological methods for biochar modification were first summarized.
- Redox-active and photocatalytic properties of biochar were emphasized.
- Adsorption, reduction, electron shuttle, and photocatalysis were main mechanisms for Cr removal by biochar.
- Interfering species influencing Cr immobilization capacity of biochar were discussed.

Journal Pre-proof

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: