Review

Recent advances of biochar materials for typical potentially toxic elements management in aquatic environments: A review

Rui Deng [a, b], Danlian Huang [a, b, *], Jia Wan [a, b], Wenjing Xue [a, b], Xiaofeng Wen [a, b], Xigui Liu [a, b], Sha Chen [a, b], Lei Lei [a, b], Qing Zhang [a, b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha, Hunan, 410082, China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, Hunan, 410082, China

ARTICLE INFO

ABSTRACT

Pristine biochar, a low-cost, sustainable and environmentally friendly material, has been regarded as an effective potentially toxic elements scavenger for many years. However, with the development of urbanization and industrialization, more types and quantities of potentially toxic elements are discharged into the environment indiscriminately, which has already exceeded the limit of pristine biochar as potentially toxic elements scavenger. Therefore, designed biochar with higher surface area, more functional groups, and higher potentially toxic elements scavenging efficiency has been concerned by researchers. Herein, the review begins with the fundamental aspects of pristine biochar fabrication, including pyrolysis, hydrothermal carbonization and some other strategies. Then the synthetic methods of designed biochar were presented to develop to control the surface morphology, functional groups and some other phy-chemical properties based on some physical and chemical design, which were more beneficial for potentially toxic elements scavenging compared with pristine biochar. Most importantly, the latest advances in biochar materials for typical contaminated potentially toxic elements (lead, cadmium, chromium, arsenic, mercury, copper, and zinc) in aquatic environments have been specifically and comprehensively performed to deeply investigate their involved mechanisms. Finally, future directions and potential challenges for this emerging frontier are discussed. It is believed that this review can afford powerful influences on the development of biochar technologies for potentially toxic elements scavenging in both experiment research and large-scale practical applications.

© 2019 Elsevier Ltd. All rights reserved.

Contents

* Corresponding author. College of Environmental Science and Engineering, Hunan University, Changsha, 410082, China.
  E-mail address: huangdanlian@hnu.edu.cn (D. Huang).

1. Introduction

Potentially toxic elements (PTEs) contamination are the environmental issue of global concern which can be originated from experimental research (spent catalysts and catalytic converters), industrial manufactures (electronic waste, smelting, and mining), agriculture activities (fertilizer and pesticide), and anthropogenic activities (domestic waste and sewage) (Wang and Wang, 2019). PTEs entering into the environment may threaten humans and animals through the food chain due to its high toxicity (Kobielska et al., 2018). For instance, cadmium (Cd) can cause kidney damage and prostate cancer (Huang et al., 2018b) and lead (Pb) can result in proximal renal tubular damage and anaemia (Inyang et al., 2016). Therefore, it is much urgent to seek more effective methods to control PTEs contamination.

As shown in Fig. 1, the number of index journal publications concerning PTEs treatment by biochar materials has increased year by year, indicating that the use of biochar materials to alleviate PTEs contamination remains a hot topic and future trend. Reportedly, there were some strategies for pristine biochar (PBC) fabrication, such as pyrolysis (Ahmad et al., 2018), hydrothermal carbonization (HTC) (Fang et al., 2018), gasification (You et al., 2018), and flash carbonization (Uchimiya et al., 2015) (Fig. 2). However, the most commonly used methods for preparing biochar for PTEs contaminants treatment were pyrolysis and HTC (Table S1). The pyrolysis referred to the process of converting biomass into charcoal, liquid, and gas by thermochemical conversion under anaerobic and anoxic conditions, which could be divided into slow pyrolysis (a few hours to a few days, $5-10$ °C min^{-1}) and fast pyrolysis ($0.5-2$ s, $1000-10,000$ °C s^{-1}) according to residence time and heating rate (Yang et al., 2019b). Slow pyrolysis was the most frequently-used PBC fabrication strategy for PTEs scavenging due to its low

process requirements, low-cost, and high biochar yields. Besides, high porosity, abundant functional groups and larger specific area by pyrolysis were beneficial for the scavenging of PTEs (Shaheen et al., 2018). Compared with pyrolysis, hydrothermal carbonization (HTC) can use some wet feedstocks (sewage sludge, municipal solid wastes, or agricultural wastes) without pre-drying and usually reacted in water for 30 min to 16 h at low temperature (from 150 °C to 350 °C). What's more, hydrochar produced by HTC usually possessed irregular surface, much more O-containing functional groups and higher cation exchange capacity (CEC) which was significantly important for PTEs adsorption (Kambo and Dutta, 2015). But the HTC is still in its early stage of development and HTC reaction usually needs to be carried out in high pressure reactor, which cannot be produced in large quantities like pyrolysis, due to high pressure and higher cost. Hence, the application of HTC to produce biochar for PTEs scavenging is not as extensive as that of pyrolysis at present.

However, with the development of urbanization and industrialization, more and more kinds of PTEs have been discharged into the environment indiscriminately, which has already exceeded the limit of PBC as PTEs scavenger (Tan et al., 2015). Traditional pyrolysis strategies have been unable to meet the requirements for the preparation of biochar for PTEs treatment. Therefore, research interests and efforts are devoted to exploring new strategies to improve the efficiency of PTEs scavenging by biochar materials (Wang et al., 2018a). Designed biochar (DBC) is followed with interest by researchers due to its enhanced physicochemical properties and higher scavenging efficiency for PTEs (Sizmur et al., 2017). Previous literatures have reported many strategies for DBC fabrication, for example, acid (HNO$_3$, H$_3$PO$_4$, H$_2$SO$_4$) (Jin et al., 2018; Lau et al., 2017; Peng et al., 2017), alkali (KOH, NaOH, Na$_2$CO$_3$, K$_2$CO$_3$) (Dehkhoda et al., 2016; Demiral and Uzun, 2010; Feng and Zhu, 2018), and some oxidizing agent (H$_2$O$_2$, KMnO$_4$) (Li et al., 2017; Wongrod et al., 2018) design. Additionally, magnetic biochar which can easily separate from aqueous solution to avoid secondary pollution (Wu et al., 2018) and some physical modification strategies (Rajapaksha et al., 2015) have been also concerned by researchers. Most importantly, the carbonaceous nanocomposites combined the advantages of biochar and nanomaterials have also attracted the attention of researchers in recent years (Tan et al., 2016b).

Numerous studies have put a spotlight on biochar materials for the scavenging of contaminants in aquatic environments, but attention to "designed biochar" for contaminants management is not fully matured, especially for "potentially toxic elements" (Premarathna et al., 2019). Most of them focused on the adsorption capacity of biochar materials for organic or inorganic contaminants, such as biochar modification potential (Rajapaksha et al., 2016), biochar application in stormwater (Mohanty et al., 2018), biochar for drinking-water purification (Palansooriya et al., 2019), and biochar-supported nZVI (Wang et al., 2019). At present, less (or no) reviews have concerned the biochar materials in PTEs treatment sorted according to the targeted PTEs, the applications of biochar materials and their involved mechanisms. Therefore, the overall objective of this review is to specifically and comprehensively
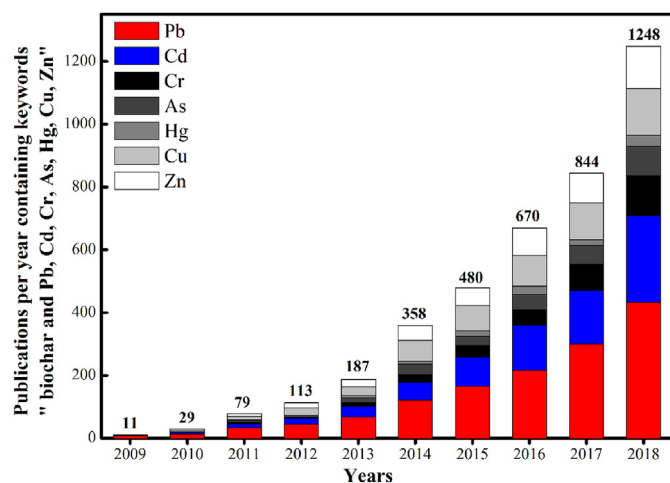

Fig. 1. Evolution of the number of publications on indexed journals (according to ISI Web of Science™) containing the keywords "biochar" and "lead (Pb)", "cadmium (Cd)", "chromium (Cr)", "arsenic (As)", "mercury (Hg)", "copper (Cu) and zinc (Zn)" and between 2009 and 2018, respectively.
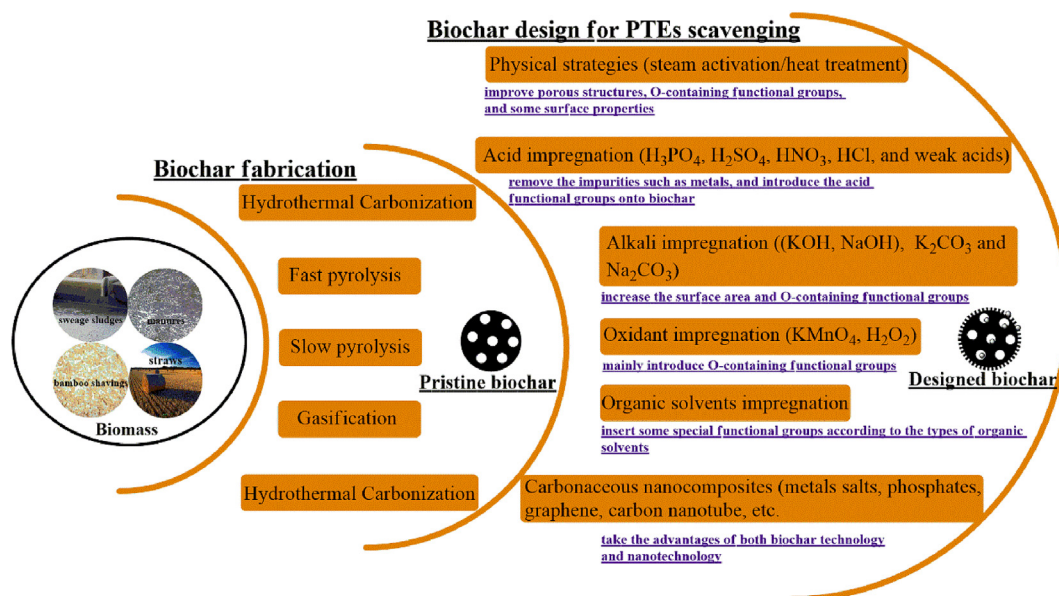
Fig. 2. The kinds of strategies of pristine biochar and designed biochar and their improvements of properties for PTEs scavenging.

perform the knowledge gap surrounding PBC and DBC, especially for their application and mechanisms of typically PTEs (Pb, Cd, chromium (Cr), arsenic (As), mercury (Hg), copper (Cu), and Zinc (Zn))) in aquatic environments. Comprehensive summaries of biochar materials fabrication and design, the latest applications of PBC and DBC for Pb, Cd, Cr, As, Hg, Cu, and Zn scavenging in environments and their involved mechanisms, as well as the possible future direction and challenges of biochar materials are provided in this review. It is foreseeable that this review can establish a powerful connection between experiment research and practical applications of biochar materials.

2. Methods

This review searched the literature published in the database in the past decade, including Web of science, Baidu and Google scholar. Furthermore, the criteria of this review for selecting literature were only peer-reviewed journals, which must be written in English. The initial search key words were "biochar" and "potentially toxic elements". The "potentially toxic elements" were classified as "lead", "cadmium", "chromium", "arsenic", "mercury", "copper", and "zinc" according to the structure of this review paper. The study has carefully examined the focus of the published comments on biochar materials and quoted them where appropriate, without repeating their conclusions. Some articles were mentioned several times because they may belong to several parts of this article at the same time. This review has extracted numerous recent literatures data and compared them to address the problems of the PTEs treatment from aquatic environment by biochar materials, presenting it in a clearer and more comprehensible manner. Based on the comparison, the study sequentially put forward the possible reasons and suggestions in biochar materials for PTEs management.

3. Synthetic strategies of designed biochar

Traditional fabrication strategies for PBC can no longer meet the scavenging of increasing PTEs. This is necessary to tailor the synthesis of biochar for selective scavenging of different PTEs. As the development of biochar technologies, a variety of biochar design strategies are emerging in an endless stream. This section mainly discussed some frequently-used strategies for DBC fabrication. Representative and more effective strategies for DBC preparation for PTEs scavenging were shown in Fig. 2. The recently typical applications of DBC for PTEs scavenging from aquatic environment were displayed in Table S2.

3.1. Few common physical strategies

Porous structures and O-containing functional groups of biochar such as, −COOH, carbonyl, and phenolic-OH groups, played a crucial role in PTEs scavenging. Steam activation which can mainly improve these properties of biochar to promote PTEs adsorption was commonly used for biochar design before. The feedstocks were firstly pyrolyzed at a temperature from 300 °C to 700 °C for 1−2 h under the condition of limited oxygen and then further pyrolyzed at a higher temperature of 800 °C−900 °C for 30 min to 3 h within steam pass (2.2 mL min^{-1} to 5 mL min^{-1}) (Rajapaksha et al., 2015). Additionally, although the steam was a weaker oxidant, it increased the hydrophilicity of biochar which can also promote the PTEs adsorption.

As for heat treatment, the feedstocks were firstly heated to 800 °C−900 °C for 1−2 h, subsequently aerated hydrogen, air or argon. This method can usually increase surface hydrophobicity of biochar and make biochar materials more dispersed in aqueous solution which can improve the area of contact between sorbent and sorbate, eventually providing more adsorption sites for PTEs (Li et al., 2014). However, these physical strategies possessed the disadvantages of cumbersome operation and harsh reaction conditions, they were soon eliminated with the advance of biochar technology. Researchers are looking for better strategies to design biochar and some chemical strategies are gradually being noticed by researchers.

3.2. Some typical chemical strategies

As for different PTEs, various chemical strategies have been developed for the design of biochar. Acid design is one of the most hackneyed chemical strategies which can remove the impurities such as metals, and introduce the acid functional groups onto biochar surface. Some common acids have been used for the

fabrication of DBC, including H_3PO_4, H_2SO_4, HNO_3, HCl, and weak acids (oxalic acid and citric acid) (Fang et al., 2017). Different acids can target different PTEs. As for Cd(II) and Cu(II), a H_3PO_4 designed biochar was fabricated and the results showed that the surface area and the contents of O-containing functional groups (-COOH and −OH) were highly improved, showing a remarkable scavenging efficiency of Cd(II) and Cu(II) from aqueous solutions. The FTIR analysis indicated that the phosphorus-containing groups (P=O and P=OOH) were complexed with Cd(II) and Cu(II) which highly improve the adsorption capacity of DBC (Peng et al., 2017). Analogously, some carboxylic, lactonic, phenolic, and carbonylic groups were be observed on the surface of HNO_3 designed biochar (Li et al., 2014). As for Hg, HCl-DBC might be a better selection which can form C−Cl groups on the surface of biochar to act as activated sites to promote Hg scavenging (Wang et al., 2018c). Moreover, the carboxyl group can be introduced onto the surface of biochar by esterification with some weak acids. Various acids made different intensity of the carboxyl groups which approximately appeared at 1743 cm^{-1} after the biochar designed by citric, tartaric, and acetic acids, and the intensity were in following order: BC-Citric > BC-Tartaric > BC-Acetic > PBC (Sun et al., 2015b).

Compared with acids, the bases design were mainly to increase the surface area and O-containing functional groups of biochar for PTEs scavenging. Some strong bases, KOH, NaOH, and weak bases (K_2CO_3 and Na_2CO_3) have also been used for the fabrication of DBC by researchers for many years (Sun et al., 2015a). For example, Jin et al. (2016) reported that biochar designed by KOH could increase the surface area (from 14.4 to 49.1 $m^2\ g^{-1}$) and the O-containing functional groups (O−H, C−O, C=O, and −COOH) of biochar, which eventually improved the maximum adsorption capacity of Cu (II) (50.71 mg g^{-1}). Besides, ion exchange was an important mechanism of PTEs scavenging. Hence, how to design biochar to improve CEC for PTEs scavenging was more vital. Ding et al. (2016) fabricated a NaOH designed biochar for some bivalent PTEs scavenging (Pb(II), Cd(II), Cu(II), and Zn(II)). Apart from the surface area (873.0 $m^2\ g^{-1}$) and the surface O-containing functional groups (-COOH and −OH) were increased compared with PBC, the CEC of the DBC (124.5 cmol kg^{-1}) was triple than PBC (45.7 cmol kg^{-1}). All the improved performance increased adsorption capacities of Pb(II), Cd(II), Cu(II), and Zn(II) by 2.6−5.8 times compared with PBC. Besides, some weak base (Na_2CO_3 and K_2CO_3) were acted as activating agents to produce DBC, which could also improve the surface area of biochar. The results showed that the highest surface areas of the two DBC were 1579 and 1596 $m^2\ g^{-1}$, and the total pore volumes were 0.8859 and 0.8296 $cm^3\ g^{-1}$ for Na_2CO_3 and K_2CO_3 (Demiral and Uzun, 2010).

O-containing functional groups of biochar usually possessed a strong affinity for PTEs. Since the mechanisms of electrostatic attraction, ion exchange, and complexation of PTEs scavenging by biochar were all associated with O-containing functional groups. Therefore, how to tailor the synthesis of biochar to improve the scavenging efficiency of PTEs were also concerned by researchers in recent years. Some strong oxidants, such as H_2O_2 (Sun et al., 2018) and $KMnO_4$ (An et al., 2019), have been used to design biochar which can improve the O-containing functional groups on the surface of biochar to enhance the adsorption performance for PTEs. For example, Wang et al. (2015) used $KMnO_4$ to pre-treating hickory wood and then pyrolyzed at 600 °C. Because of the strong oxidation of $KMnO_4$, more surface O-containing functional groups (-COOH, −OH, and MnO_x) were detected after design, and the surface area was doubled. Therefore, the adsorption efficiency of Pb(II), Cu(II), and Cd(II) were greatly improved due to these performance improvements compared with PBC. Compared with $KMnO_4$, H_2O_2 was a relatively inexpensive and clean strong oxidant. Reportedly, biochar treated with H_2O_2 can also increase O-

containing functional groups, especially −COOH, which in turn increase the adsorption efficiency of Pb(II), Cu(II) and Cd(II) from wastewater (Xue et al., 2012).

Additionally, some special functional groups also played a crucial part in the scavenging of PTEs. Hence, some chemical organic solvents which possessed special functional groups have also been used to design biochar for PTEs scavenging. For example, chitosan, which was a food additive, was used to fabricate DBC by researchers. The impregnation of chitosan could introduce amine functional groups and then enhance its efficiency for Pb(II) scavenging (Zhou et al., 2013). Similarly, Zhang et al. (2015) fabricated a β-cyclodextrin-chitosan biochar to scavenge Cr(VI) from aqueous solution. Amino and carboxyl groups introducing by chitosan highly improved the maximum scavenging efficiency of the DBC with about 93%, which was higher than PBC (about 27%). Besides, Deng et al. (2017) used pyromellitic dianhydride (PMDA) to design biochar for Cd(II), Cu(II), and Pb(II) scavenging which introduced much functional groups, and they reported that the N−C=O groups were mainly for Pb(II) scavenging, C=C groups for Cd(II), and carbonyl groups for Cu(II). Additionally, Ma et al. (2014) fabricated a polyethylenimine (PEI) designed biochar. Compared with PBC, the maximum adsorption capacity of DBC was 435.7 mg g^{-1} while PBC was only 23.09 mg g^{-1} which might be due to the appearance of abundant amino groups on biochar surface after design.

These typical chemical strategies could all improve the properties of biochar and promote the scavenging efficiency of PTEs, but some of them only used in laboratory due to the possibility of secondary contamination and high cost. For example, the use of some strong acids and bases may change the pH of the environment and destroy the ecological balance. The cost of strong oxidants is high and its environmental toxicological effects have not been studied thoroughly. The eco-toxicity of these chemical strategies was not neglected. Consequently, finding more eco-friendly, low-cost and high-efficiency chemical solvents to design biochar are still significant. Carbonaceous nanocomposites gradually appeared in people's field of vision.

3.3. Carbonaceous nanocomposites

Nanomaterials have been widely used in PTEs processing and some characteristics of nanomaterials are particularly important for the scavenging of PTEs. With the development of biochar technology and nanotechnology, how to combine biochar technology with nanotechnology to remove PTEs becomes the research hot spot. So carbonaceous nanocomposites appeared and they usually meant that biochar combined with certain nanomaterials to obtain new composites, which could introduce nanoparticles on the surface of biochar and both possessed the advantages of biochar and nanomaterials (Tan et al., 2016b). The main mechanisms of different types of carbonaceous nanocomposites for PTEs scavenging were displayed in Fig. 3. Reportedly, the magnetic biochar were the most common carbonaceous nanocomposites, which were usually synthesized by iron or iron oxides impregnation with biomass, such as zero-valent iron (ZVI, Fe(0)), Fe_2O_3, Fe_3O_4, and Fe^{2+}/Fe^{3+} (Trakal et al., 2016). As for Pb(II) and Cd(II), cation exchange was an important mechanism. Biochar pre-treated by Fe^{2+} solutions and then through microwave heating generated magnetic iron oxide particles biochar surface. After design, the CEC value of the magnetic biochar was significantly increased due to the presence of Fe oxides on the surface biochar which significantly enhanced the adsorption capacity of Pb(II) and Cd(II) (Trakal et al., 2016). As for Cr(VI), the reducing action was the main mechanism. Reportedly, researchers used nano zerovalent iron (nZVI) to design biochar for Cr(VI) scavenging. It was found that the C=O and C=C were formed with the C−O and COOH groups crack during the
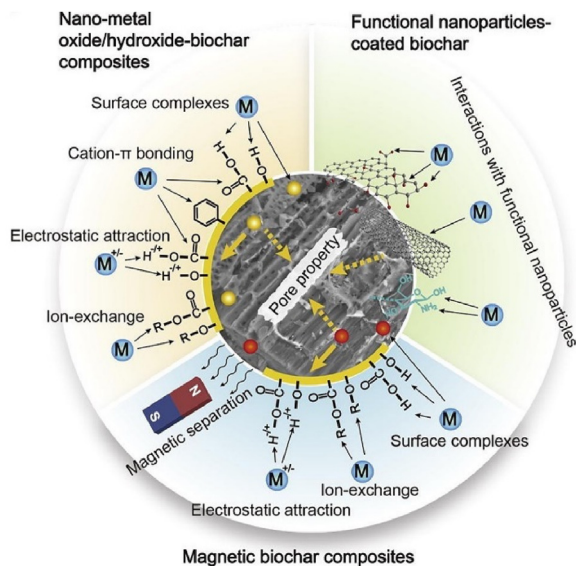
Fig. 3. The main mechanisms of different types of carbonaceous nanocomposites for heavy metals scavenging. (Adopted from (Tan et al., 2016b)).

combination of nanoparticles and biochar, indicating the C–O–Fe acted as an electron acceptor during reduction and it was important for Cr(VI) scavenging by nZVI (Zhu et al., 2017). Except for iron salts, a few other metals salts, such as $AlCl_3$ (Jiang et al., 2018), $MgCl_2$ (Xu et al., 2019b), $ZnCl_2$ (Xia et al., 2016), $CaCl_2$ (Foroutan et al., 2018), and $MnCl_2$ (Liang et al., 2017), were also used to pre-treat biomass and then pyrolyze, in which eventually formed Al_2O_3, MgO, ZnO, CaO, and MnO_x nanoparticles in the pores or on biochar surface after pyrolysis to obtain novel carbonaceous nanocomposites for PTEs scavenging. For example, a $ZnCl_2$-designed biochar possessed a larger specific surface area (516.67 m^2 g^{-1}) than PBC, and exhibited an excellent porous texture, which eventually made a great contribution to As(III) scavenging by formed the ligand exchange of Zn–O–As(III) (Xia et al., 2016). An Al_2O_3-biochar nanocomposite was fabricated by $AlCl_3$ pretreated biomass. The results displayed that the Al_2O_3 nanoparticles dispersed on biochar surface and the Al_2O_3 nanoparticles increased the reactive area and sites to scavenge PTEs from wastewater (Jiang et al., 2018).

Certain nanomaterials have been shown to have excellent repair effects for specific PTEs. For example, nano-chlorapatite has been testified to have excellent scavenging ability for Pb(II) and Cd(II), which can form stable insoluble compounds, $Pb_5(PO_4)_3Cl$ and $Cd_5(PO_4)_3Cl$ (Wan et al., 2018). But they also reported that the excess phosphorus released by nano-chlorapatite during remediation process might cause the risk of eutrophication. Therefore, Deng et al. (2019a) synthesized a novel carbonaceous nano-chlorapatite which combined biochar with nano-chlorapatite (CPBC) to scavenge Pb(II), Cd(II), and Cu(II) from aquatic environments. They found that the formation of $Pb_5(PO_4)_3Cl$, $Cd_5(PO_4)_3Cl$, and $Cu_3(PO_4)_2$ precipitates were mainly responsible for Pb(II), Cd(II), and Cu(II) scavenging. Besides, biochar-supported graphene (GO-biochar) oxide could significantly improve the Cr(VI) scavenging ability. The results indicated that the C=C, aromatic compounds, and C=O introduced by GO played an important role for Cr(VI) scavenging and the main mechanisms including three steps: firstly, adsorption of Cr(VI) by electrostatic attraction; secondly, reduction of Cr(VI) to Cr(III); thirdly, complexation with Cr(III) (Shang et al., 2016). Similarly, biochar designed by carbon nanotube (CNT) could also enhance the scavenging efficiency Pb(II) and Cd(II) (Liu et al., 2016a). What' more, Zeng et al. (2019) fabricated a MoS_2-

biochar nanocomposite and the MoS_2 nanosheets grew unevenly on the surface of biochar after its introducing which made the adsorption performance of biochar highly improve.

Each design method has its advantages and disadvantages. Carbonaceous nanocomposites can well take the advantages of both biochar and nanomaterials to enhance the PTEs scavenging. However, their eco-toxicity should be also concerned. For example, some nanomaterials contained metals might bring secondary contamination of metals. Biochar supported phosphates materials might possess eutrophication risk. Therefore, how to choose environmentally friendly and low-cost nanomaterials to prepare carbonaceous nanomaterials will be the priority of future research. But as far as it goes, these biochar design strategies were the main and efficient strategies for PTEs scavenging.

4. Biochar materials for typical PTEs contamination management

Recently, the applications of biochar materials (including PBC and DBC) on PTEs have become the research hotspot of scientists. Different PTEs usually possessed different scavenging mechanisms by biochar materials. What follows, is the most significant section of this article, approximately sorts by the frequency of biochar materials applied to typical PTEs contamination and current pollution situation of PTEs (Pb–Cd–Cr–As–Hg–Cu–Zn), then detailedly discussing the findings by PBC and DBC of each PTEs and their involved mechanisms one by one. Fig. 4 demonstrated the main mechanisms of PTEs scavenging by different biochar design strategies.

4.1. Pb (II)

Pb(II) entering into human body through the food chain would result in various diseases, even death (El-Banna et al., 2019). Therefore, biochar materials as their eco-friendly, low cost, and high adsorption performance were used for Pb(II) scavenging in recent years. Shi et al. (2019) fabricated biochars at 300 °C, 500 °C, and 700 °C (BC300, BC500, and BC700) by rice husk for Pb(II) scavenging. It was found that temperature had a great influence on the properties of this biochar. The surface area and pH were visibly increased from 0.632 to 193.149 m^2 g^{-1} and 7.13 to 9.80 with the increasing temperature from 300 °C to 700 °C, while the carboxyl decreased. The adsorption capacity of Pb(II) was also increased as the temperature rose which indicated that temperature was quite vital for Pb(II) adsorption by PBC. Besides, they also found that the cation exchange was the main mechanism for BC300, while the precipitation of the formation $Pb_3(CO_3)_2(OH)_2$ for BC500 and BC700. Analogously, Shen and co-workers also reported the similar circumstances. They used rice straw to produce biochar at 300 °C, 500 °C, and 700 °C for Pb(II) scavenging. They found that higher pyrolysis temperature can promote biochar to remove Pb(II) faster and the precipitation was the dominating mechanism for Pb(II) scavenging which can make Pb(II) more stable as the pyrolysis temperature rose (Shen et al., 2019).

As for DBC in Pb(II) scavenging, a novel biochar which hybridized with CeO_2–MoS_2 (CMMB) was used to scavenge Pb(II) from wastewater (Li et al., 2019). This design greatly improved its adsorption performance compared with PBC. The dominating mechanisms of Pb(II) scavenging were a combination process of electrostatic attraction, Cπ–Pb(II) bond interaction, complexation, and physical adsorption. Else oxidized biochar which designed by H_2O_2 and $KMnO_4$ obviously improved the sorption ability of Pb(II), reducing the bioavailability of Pb(II) in hydroponically grown plants which might be due to the more O-containing functional groups (El-Banna et al., 2018). In addition, as the retrievability and
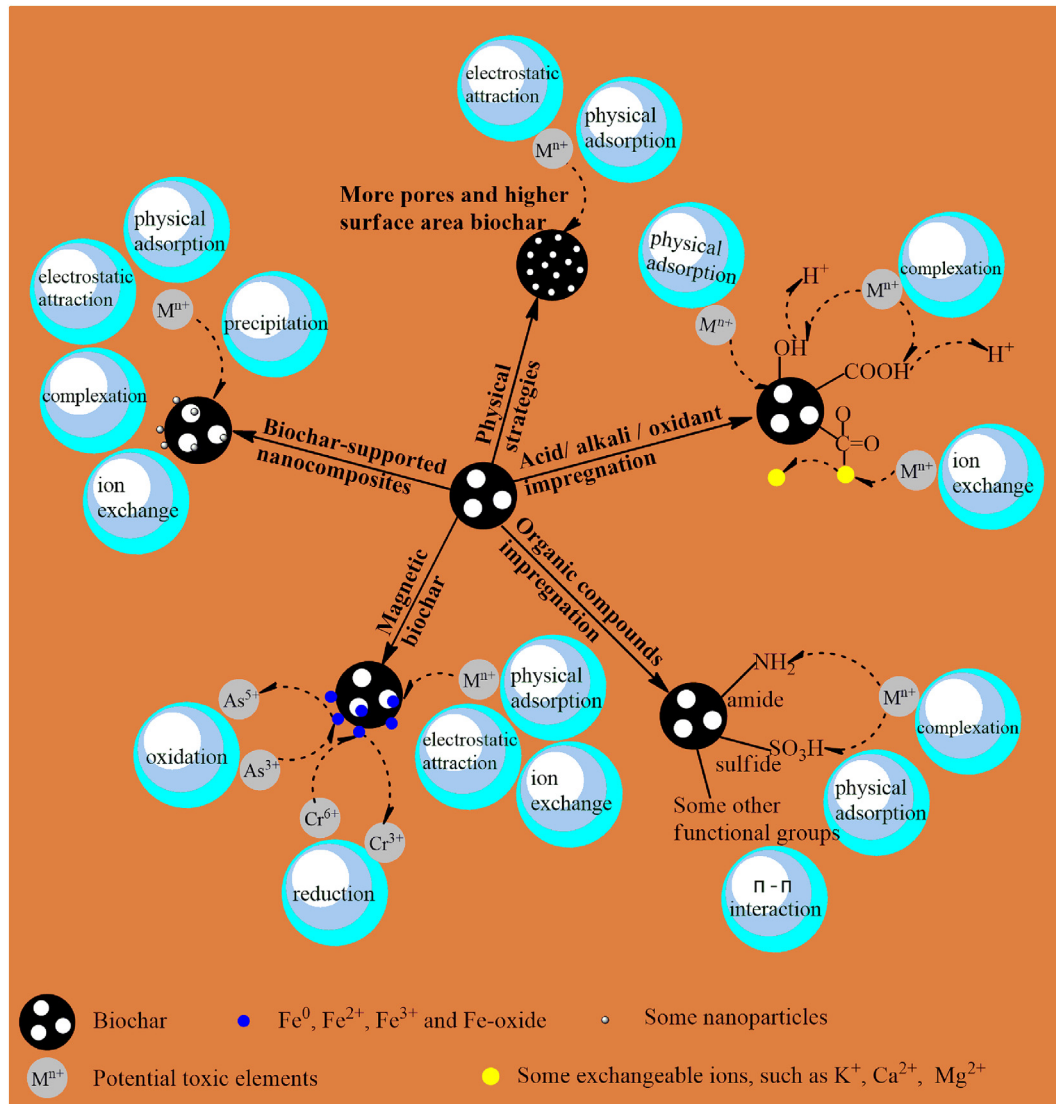
Fig. 4. Schematics of the properties of biochar after design and the involved mechanisms of PTEs scavenging by designed biochar with kinds of strategies.

reusability of iron-based nanoparticles, it is easier to separate them from wastewater after remediation which can avoid environmental hazards and toxicity of materials (Lei et al., 2018). For example, the contamination of groundwater of PTEs were serious, researchers used nZVI to design biochar for PTEs adsorption which cannot only improve the adsorption performance of biochar, but also can separate them from the groundwater (Yang et al., 2018). They found that possible mechanism for Pb^{2+} scavenging by nZVI-biochar included two key steps: (1) free Pb(II) were adsorbed by electrostatic attraction from wastewater to the active sites of nZVI-biochar; (2) then Pb(II) was reduced to Pb(0) by metallic iron. Besides, the precipitation and surface complexation were also involved. In 2019, this group used electrochemical methods for the fabrication of thorn-like iron-based biochar composites. This method introduced more O-containing functional groups onto biochar surface, which were mainly responsible for Pb(II) adsorption from wastewater (Yang et al., 2019a).

Furthermore, phosphate materials were used for Pb(II) scavenging due to their excellent cooperation ability with Pb(II) in environments (Huang et al., 2018a). Recently, a novel biochar-orthophosphate composite was successfully fabricated by

$Ca(H_2PO_4)_2 \cdot H_2O/KH_2PO_4$ pre-impregnating with rice straw (WBC−Ca/WBC-K) for Pb (II) scavenging from aqueous solutions (Gao et al., 2019). The results displayed that the maximum sorption capacities of Pb(II) of WBC-Ca and WBC-K were 566.3 and 1559 mmol kg^{-1} which approximately more than 3 and 8-folds than PBC. The formation of Pb-precipitates, such as, $Pb_5(PO_4)_3Cl$, $Pb_2P_2O_7$, and $Pb_{n/2}(PO_3)_n$ might be responsible for Pb(II) scavenging. Analogously, a novel carbonaceous nano-chlorapatite was synthesized to scavenge Pb(II) from aqueous solutions and the maximum scavenging efficiency of Pb(II) was up to 90.37%. The formation of pyromorphite $(Pb_5(PO_4)_3Cl)$ through precipitation might be the main mechanism of this designed biochar for Pb (II) scavenging (Eq. (1)) (Deng et al., 2019b).

$$5Pb^{2+} + 3H_2PO_4^- + Cl^- \rightarrow Pb_5(PO_4)_3Cl\downarrow \qquad (1)$$
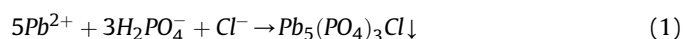
4.2. Cd(II)

Cd(II), another high toxicity bivalent PTE, was similar to Pb(II) and also possessed hydrophilia, high toxicity, persistence and

difficult mobility in environment (Huang et al., 2016). Therefore, Pb(II) and Cd(II) also displayed similar scavenging mechanisms when they were treated by biochar materials. As for PBC, Melo et al. (2013) synthesized biochars at 300 °C, 500 °C and 700 °C for Cd(II) scavenging and found that the cation-π interaction controlled the Cd(II) scavenging at lower pyrolytic temperature (300 °C) while precipitation became the predominant mechanism at high pyrolytic temperature (700 °C). Apart from temperature, pH was another critical factor which can highly affect Cd(II) scavenging efficiency. As the pH was in the range of 3−5, the Cd(II) scavenging rate was obviously increased, but the influences tended to be gentle when the pH was higher than 5 (Li et al., 2018). Besides, it was also reported that different feedstocks can also influence the Cd(II) scavenging efficiency by biochar. Wang et al. (2018b) fabricated three types of biochars with bamboo, corn straw, and pig manure for Cd(II) scavenging. They found that the pig manure biochar exhibited best adsorption efficiency for Cd(II) which was mainly attributed to the more O-containing functional groups on pig manure biochar. What's more, precipitation and cation exchange were also involved in Cd(II) scavenging by these biochars.

Except for PBC, more and more DBC were used for Cd(II) scavenging. Tan et al. (2017a) pre-treated rice straw with Fe^{2+}/Fe^{3+} and then pyrolyzed at 400 °C to obtain a novel DBC. The maximum scavenging efficiency of Cd(II) by this DBC was up to 91%, which was much higher than that of the PBC. The $CdFe_2O_4$ appeared in the X-ray diffraction (XRD) patterns after the Cd(II) adsorption while the primary strongest magnetic biochar peak disappeared, indicating that the ion exchange was the main mechanism for Cd(II) adsorption. It also exhibited that Cd(II) can be chelated with hydroxyl (−C−OH) and carbonyl (−C=O) functional groups. In 2019, a novel carbonaceous nanocomposite combined with nano-TiO_2 and biochar via ultrasonic greatly improved the scavenging efficiency of Cd(II). The results also showed that the ion exchange and surface complexation were the main mechanisms for Cd(II) scavenging (Luo et al., 2019). Another biochar pyrolyzed under CO_2 atmosphere was also used for Cd(II) scavenging. The organic functional groups (−C−OH, −C=O, COO−) after CO_2 design can complex with Cd(II), which might be main mechanism for Cd(II) scavenging (Tan et al., 2017b). Similarly, a new class of N-doping biochar was synthesized under NH_3 atmosphere which exhibited a remarkable adsorption capacity for Cd(II) (1.76 mmol g^{-1}, 4 times than PBC) (Yu et al., 2018b). The graphitic N on biochar surface were regarded as the main contribution for the scavenging mechanisms, including cation-p bonding and complexation with graphitic-N and hydroxyl groups on biochar surface.

In conclusion, apart from physical adsorption due to the large surface area and porosity of biochar materials, the mechanisms for Pb(II) and Cd(II) scavenging usually depended on different designed strategies. Cation exchange, electrostatic attraction, complexation with functional groups, and precipitation were the common mechanisms for Pb(II) and Cd(II) scavenging by various DBC.

4.3. Cr (III, VI)

Cr was regarded as a carcinogenic, persistent, and bio-accumulative PTEs which mainly exists in two forms in natural environment: Cr(III) (Cr^{3+} cations) and Cr(VI) (CrO_4^{2-} anions) (Cho et al., 2019). Reportedly, Cr(III) is 300 times less toxic than Cr(VI), but it is eventually oxidized to Cr(VI) due to its strong oxidizing properties, which poses a terrible health risk to humans (Zhang et al., 2019).

A PBC derived from soybean and burcucumber residues were utilized for Cr(VI) scavenging. It was found that the dominating mechanism of Cr(VI) scavenging was reduction of Cr(VI) to Cr(III)

and the maximum scavenging efficiency of Cr(VI) occurred at pH values varying from 2 to 5 (Rajapaksha et al., 2018). Additionally, Ruan et al. (2019) reported that there are persistent free radicals (PFRs) on biochars which can directly or indirectly mediated $S_2O_8^{2-}$ or H_2O_2 to degrade organics/inorganics. Hence, Zhao et al. (2018) fabricated biochar at different temperatures which exhibited diverse adsorption ability of Cr(VI) with the order of 300 °C > 500 °C > 700 °C. The further electron spin resonance and free radical quenching experiments confirmed that the PFRs on biochar surface made the Cr(VI) reduce to Cr(III), and then Cr(III) can form $Cr(OH)_3$ precipitate onto biochar. Moreover, Xu et al. (2019a) reported that biochar can be regarded as both electron donor (-C-O and C=O) and electron shuttle (semiquinone-type radicals) for Cr(VI) reduction. They also confirmed that the pH values could highly influence the reduction process. The results showed that the scavenging efficiency at pH = 2 was obvious stronger than that of pH = 4. Similarly, Xu et al. (2019c) also reported that electron transfer between biochar and low molecular weight organic acid made the Cr(VI) reduce to Cr(III). Therefore, reducing Cr(VI) to Cr(III) was an extremely effective method for Cr(VI) scavenging. However, the Cr(III) scavenging after reduction is equally important. Chen et al. (2015) took advantage of municipal sewage sludge to fabricated biochar at 900 °C for the scavenging of Cr(III) and Cr(VI). By reported, biochar contained many alkaline substances which could release OH$^-$ and cause the solution pH increase. The Cr(III) was soluble at low pH, but when the pH increased to more than 5.5, the $Cr(OH)_3$ precipitation might appear. Thus the precipitation might be the main mechanism for Cr(III) scavenging after biochar addition. The study also confirmed that unreduced Cr(VI) was difficult to be adsorbed by a single biochar. Hence, it is necessary to fabricate more designed biochar to reduce Cr(VI) to further improve the scavenging efficiency of Cr(VI) contamination.

For Cr(VI) scavenging by DBC, Liu et al. (2016b) prepared a novel DBC by fast pyrolysis which embedded Ag nanoparticles into biochar (Ag@biochar) to catalyze Cr(VI) reduction. The Ag@biochar displayed a remarkable catalytic activity for the reduction of Cr(VI) to Cr(III) within 20 min in aqueous solutions. They found that the Ag nanoparticles on the surface play an important role for the reduction of Cr(VI) which followed a CO (HCOOH decomposition) reduction mechanism (Eqs. (2) and (3)). Similarly, a core-shell structure $Fe_3O_4@SiO_2−NH_2$ nanomagnetic biochar also exhibited a remarkable reduction efficiency of Cr(VI) (Shi et al., 2018). As reported, the scavenging processes of Cr(VI) by this biochar were that: 1) Cr(VI) firstly absorbed by protonated functional groups; 2) Cr(VI) was reduced to Cr(III) by electron-donor groups; 3) Cr(III) was precipitated by amine groups. Apart from this, another magnetic biochar composite which impregnated by nZVI and calcium-alginate (CA) bead (nZVI/BC/CA) was prepared for Cr(VI) scavenging (Wan et al., 2019). The results found that there was a micro-electrolysis system in the treating process. In this system, Fe provided electrons as an anode and BC or CA mainly acted as a cathode to accelerate the redox reaction of Cr(VI) to Cr(III).

$$HCOOH \rightarrow H_2O + CO \qquad (2)$$

$$2CrO_4^{2-} + 10H^+ + 3CO \rightarrow 2Cr^{3+} + 3CO_2 + 5H_2O \qquad (3)$$
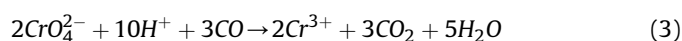
However, in addition to reduction, some other mechanisms, such as electrostatic attraction, surface complexation, ion exchange, and precipitation can also contribute to Cr(VI) scavenging. Yu et al. (2018a) fabricated a ZnO-nanoparticles designed biochar for Cr(VI) scavenging. They found that the biochar loaded with 30 wt % ZnO exhibited more than 95% scavenging efficiency of Cr(VI) and the results indicated that the precipitation between

Cr(VI) and ZnO might be the main mechanism. Besides, Huang et al. (2019a) used EDTA and Mg/Al layered double hydroxides (LDH) combined with bamboo biochar to scavenge Cr(VI) from wastewater and they found that the interaction between LDH and Cr(VI) might control the adsorption process, including surface adsorption, ion exchange and precipitation.

4.4. As (III, V)

As a kind of PTEs, the toxicity of As should also be considered since it may lead to hepatomegaly, melanosis, gastrointestinal lesion, cardiovascular diseases, and even death (Hu et al., 2015). It was similar to Cr that As also existed two main valence in environment: As(V) and As(III). Conversely, the higher valence As(V) was lower toxic and more difficult to migrate than the lower valence As(III). Thus the oxidation of As(III) into As(V) was a remarkable strategy to reduce the toxicity and detriment of As in environment (Dong et al., 2014). Reportedly, biochar derived from sugar beet tailing and Brazilian pepper contained abundant dissolved organic matter (DOM) and they showed brilliant efficiency for As(III) oxidation from aqueous solution (Dong et al., 2014). The analysis of electron spin resonance (ESR) and FTIR suggested that the DOM from biochar not only acted as an electron donor but also as an acceptor. The carboxylic groups might contribute to the oxidation and complexation of As(III). Lin et al. (2017) impregnated biochar with Fe−Mn oxides to scavenge As(III) from aqueous solution and the results demonstrated that the As3d and Fe2p regions appeared after As(III) adsorption, indicating that O-containing functional groups from the DBC promoted the conversion of As(III) into As(V). However, Niazi et al. (2018) prepared two biochars derived by perilla leaf and pyrolyzed at 300 °C and 700 °C (BC300 and BC700) for As(V) and As(III) scavenging. The adsorption affinity followed in this order: BC700 for As(III) > BC700 for As(V) > BC300 for As(III) > BC300 for As(V), indicating that the adsorption capacity of As(III) was higher than As(V) by biochar. They reported that the oxidation process of As(III) to As(V) was marginally weaker than reduction process of As(V) to As(III) since the abundant surface functional groups on biochar surface (-COOH, phenolic) acted as electron donors. Additionally, A ZVI-biochar was highly effective for As(V) scavenging. The results showed that the oxidation of Fe^0 to Fe^{3+} and reduction of As(V) to As(III) synchronized and then the As(III) was adsorbed by isomorphous substitution of As(III) for Fe^{3+} in α/γ-FeOOH with co-precipitation (Bakshi et al., 2018). In 2017, Zhou et al. (2017) fabricated a magnetic gelatin-DBC for As(V) scavenging. It was reported that As(V) mainly existed as $H_2AsO_4^{2-}$ at pH = 4 and some functional groups of the DBC were protonated and positively charged. At this time, the electrostatic attraction might control the adsorption process. Additionally, the O-contained functional groups and hydroxyl complexation between As(V) and DBC also contributed to As(V) scavenging.

Unlike Pb(II) and Cd(II), Cr and As were belong to redox-sensitive elements. The oxidation-reduction played an important role in their scavenging mechanisms. As for Cr, the reduction of Cr(VI) to Cr(III) and then complexation and precipitation with Cr(III) were the main mechanism for Cr scavenging. However, the redox process of As(V) to As(III) or As(III) to As(V) was really complex. Biochar materials treated with As usually both possessed the reduction and the oxidation process. Different designed strategies possessed different mechanisms for As scavenging.

4.5. Hg (0, II)

Hg is a special kind of PTEs which can lead to lung damage and some chronic poisoning in neurological and psychological systems when it was exposed to human (Ifthikar et al., 2018). Hg usually exists with three main valence states in the environment: elemental mercury (Hg^0) in flue gas and oxidized mercury (CH_3Hg^+ and Hg(II)) in aqueous solutions (Wang et al., 2018d). Xu et al. (2016) compared PBC and activated carbon (AC) for Hg(II) adsorption and showed that although AC possessed much higher specific surface area than biochar, PBC exhibited more remarkable efficiency than AC for Hg(II) scavenging (approximately 6.5 times than AC), suggesting that the surface area didn't control the Hg(II) scavenging by biochar. The results also indicated that Hg(II) adsorption by PBC was mainly controlled by Hg-π binding which induced by C=C or C=O and (-COO)$_2$Hg. But the dominating mechanism of AC was the formation of (-O)$_2$Hg by complexation due to the O-containing functional groups (-COOH, phenolic hydroxy, and carbonyl). In 2019, a sulfurized biochar (SB) was fabricated to scavenge Hg(II). The interactions with C=C, COH, and COO mainly controlled the adsorption process of Hg(II) by the DBC while the formation of thiophenic and C-SO$_x$-C were also responsible for Hg(II) scavenging (Park et al., 2019). Moreover, a graphene loaded biochar was fabricated by researchers for Hg(II) scavenging from aqueous solutions. Characterization analysis revealed that the surface complexation with the functional groups (e.g. C=C, C=O, C−O, and −OH) on the DBC surface were responsible for Hg(II) scavenging (Tang et al., 2015). Furthermore, Huang et al. (2019b) used 3-mercaptopropyltrimethoxysilane to designed biochar for Hg(II) and CH_3Hg^+ scavenging from aqueous solution. They found that the active sites (-SH, −OH, −COOH, and −NH$_2$) on biochar surface played an important role in Hg(II) and CH_3Hg^+ scavenging by ligand exchange and surface complexation, especially −SH. Tan et al. (2016a) compared three DBC, Na$_2$S-biochar (SC), KOH-biochar (KC), and AC for Hg(II) scavenging from aqueous solutions. The SC exhibited best adsorption capacity for Hg(II) due to the precipitation of HgS and the O-containing functional groups on the DBC.

From the above, the major mechanisms of Hg(II) was surface complexation with the functional groups, especially O-containing functional groups. But the physical adsorption and little precipitation (HgS) also involved in Hg(II) scavenging from aqueous solutions.

4.6. Cu(II) and Zn(II)

Cu(II) and Zn(II) were both the trace elements which were needed by the human body and they usually existed in divalent valence in environment. However, excessed Cu(II) and Zn(II) also might be harmful to human health (Cibati et al., 2017). Song et al. (2019) prepared a novel artemisia argyi stem biochar at 300 °C, 450 °C, and 600 °C for Cu(II) scavenging. The results showed that ion exchange and chemical bonding effects with hydroxyl, lactone, and carboxyl might be the main mechanisms for Cu(II) scavenging. Yang and Jiang (2014) synthesized a novel DBC with amino modification to scavenge Cu(II) from aqueous solution. The amino-modified biochar demonstrated a remarkable scavenging efficiency for Cu(II) scavenging which was nearly 5-folds of PBC. XPS and FTIR results suggested that the functional groups on biochar surface were chemically bound with the amino groups, suggesting that the strong complexation between Cu(II) and amino groups might be the main mechanism for Cu(II) scavenging. Jiang et al. (2016) fabricated two biochars for Cu(II) and Zn(II) scavenging and further evaluated the influence of sulphate-induced salinity and acidic pH. The adsorption performance for Cu(II) and Zn(II) was greatly affected by the surface alkalinity, the negative charge of biochar surface and the CEC. The adsorption process was a pH-dependent process which can obviously increase the adsorption capacity of Cu(II) and Zn(II) when the pH was rising to 6. Additionally, a multifunctional iron-biochar composite (Fe-biochar) was
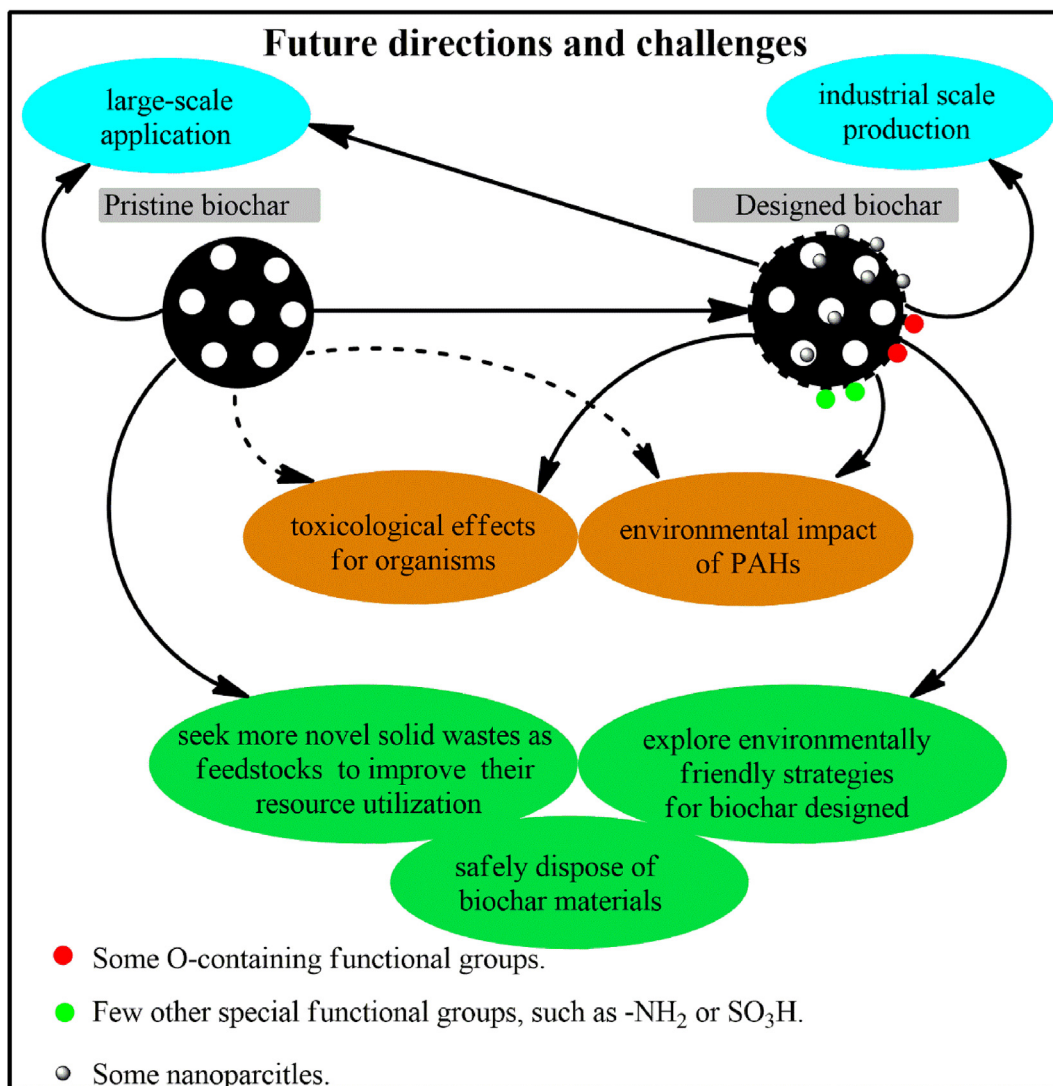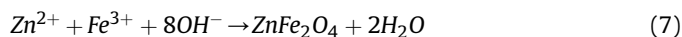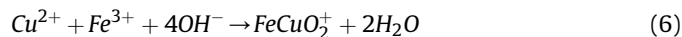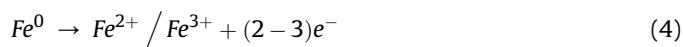
Fig. 5. Future directions and changes of biochar materials.

produced for Cu(II) and Zn(II) scavenging. They stated briefly that Fe^0 accelerated Cu(II) scavenging by reduction and complexation with the colloidal Fe^{3+} (Eqs. (4)–(6)). As for Zn(II), the main mechanisms were surface adsorption and complexation with the colloidal Fe^{3+} (Eq. (7)) (Sun et al., 2019). Besides, biochar and AC were compared to scavenge Zn(II) from aqueous solution and it was found that biochar exhibited higher efficiency for Zn(II) scavenging than activated carbon. The results showed that Zn(II) were major complexed with some ionized O-containing functional groups (such as −COOH, −OH, and phenol (R−OH) groups) by ion exchange (Zamani et al., 2017). What's more, Ding et al. (2016) used NaOH modified biochar to scavenge Cu(II) and Zn(II) from wastewater and the results displayed that NaOH could promote the surface area, CEC, and O-containing functional groups of biochar which played an important role for Cu(II) and Zn(II) scavenging.

$$Fe^0 \rightarrow Fe^{2+} / Fe^{3+} + (2-3)e^- \tag{4}$$

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \tag{5}$$

$$Cu^{2+} + Fe^{3+} + 4OH^- \rightarrow FeCuO_2^+ + 2H_2O \tag{6}$$

$$Zn^{2+} + Fe^{3+} + 8OH^- \rightarrow ZnFe_2O_4 + 2H_2O \tag{7}$$

Cu(II) and Zn(II) were similar with Pb(II) and Cd(II) since they are bivalent PTEs which also possessed similar mechanisms. Nevertheless, studies on Cu(II) and Zn(II) were relatively rare due to their much lower toxicity than Pb(II) and Cd(II). The hazards of Cu(II) and Zn(II) is also not neglected with the development of urbanization and industrialization.

5. Conclusions and future directions

Aquatic environments are the main "storage" area for PTEs. It is utmost important to seek more effective and eco-friendly strategies for the scavenging of PTEs from aquatic environments. Biochar materials have become the "star" for PTEs treatment due to their low-cost, large specific surface area, porous structure, abundant functional groups, and adjustable performance. This review chiefly summarized numerous recent literatures to address the problems of the PTEs treatment from aquatic environment by biochar

materials, and focuses on studying existing data and presenting it in a clearer and more comprehensible manner. The article was primarily introduced how to tailor the synthesis of biochar materials for improved/selective scavenging of different PTEs and then mainly sorted according to the targeted PTEs, the applications of biochar materials and their involved mechanisms. The purpose of this review is to provide a panoramic view about this research field and an easily accessible summary of available data. It is evident that this steadily growing field has a considerable number of available strategies for biochar design, such as physical and chemical strategies to elevate the properties of PBC, especially for carbonaceous nanocomposite which can possessed the advantages of biochar and nanomaterials for PTEs scavenging. The dominating mechanisms for this typical PTEs scavenging by biochar materials including: physical absorption, electrostatic interaction, ion-exchange, surface complexation with functional groups, precipitation, and reduction and oxidation for some redox-sensitive elements.

Although biochar materials have been concerned for PTEs scavenging for many years, research in this field is also at the developmental stage. There are many improvements which should be required before the technology can be completely applied beyond laboratory research. Fig. 5 simply displayed the future directions and challenges of biochar materials. Further research should be directed to: 1) seek more novel solid wastes as feedstocks of biochar fabrication for PTEs scavenging to greatly reduce solid waste in large scale and improve its resource utilization; 2) explore more effective and environmentally friendly strategies for biochar design for PTEs scavenging; 3) concern the environmental impact of polycyclic aromatic hydrocarbons (PAHs) produced during biochar pyrolysis which might be released into environments to influence the human and organisms; 4) focus on the toxicological effects for organisms of PBC and DBC in large-scale application, for example, containing metals or other environmental-hazardous might have an adverse effect on living things in the environment; 5) find suitable approaches to safely dispose the biochar materials after the adsorption PTEs and avoid the accumulation of biochar materials in the environment with a large scale application and the rerelease of PTEs into environment.

Declaration of competing interest

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.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.119523.

References

Ahmad, Z., Gao, B., Mosa, A., Yu, H., Yin, X., Bashir, A., Ghoveisi, H., Wang, S., 2018. Removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions by biochars derived from potassium-rich biomass. J. Clean. Prod. 180, 437−439.

An, Q., Jiang, Y.Q., Nan, H.Y., Yu, Y., Jiang, J.N., 2019. Unraveling sorption of nickel from aqueous solution by KMnO$_4$ and KOH-modified peanut shell biochar: implicit mechanism. Chemosphere 214, 846−854.

Bakshi, S., Banik, C., Rathke, S.J., Laird, D.A., 2018. Arsenic sorption on zero-valent iron-biochar complexes. Water Res. 137, 153−163.

Chen, T., Zhou, Z., Xu, S., Wang, H., Lu, W., 2015. Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge. Bioresour. Technol. 190, 388−394.

Cho, D.W., Yoon, K., Ahn, Y., Sun, Y., Tsang, D.C.W., Hou, D., Ok, Y.S., Song, H., 2019. Fabrication and environmental applications of multifunctional mixed metal-biochar composites (MMBC) from red mud and lignin wastes. J. Hazard Mater. 374, 412−419.

Cibati, A., Foereid, B., Bissessur, A., Hapca, S., 2017. Assessment of Miscanthus× giganteus derived biochar as copper and zinc adsorbent: study of the effect of pyrolysis temperature, pH and hydrogen peroxide modification. J. Clean. Prod. 162, 1285−1296.

Dehkhoda, A.M., Gyenge, E., Ellis, N., 2016. A novel method to tailor the porous structure of KOH-activated biochar and its application in capacitive deionization and energy storage. Biomass Bioenergy 87, 107−121.

Demiral, H., Uzun, I., 2010. Preparation and characterization of activated carbons from poplar wood (Populus L.). Surf. Interface Anal. 42 (6−7), 1338−1341.

Deng, J., Liu, Y., Liu, S., Zeng, G., Tan, X., Huang, B., Tang, X., Wang, S., Hua, Q., Yan, Z., 2017. Competitive adsorption of Pb (II), Cd (II) and Cu (II) onto chitosan-pyromellitic dianhydride modified biochar. J. Colloid Interface Sci. 506, 355−364.

Deng, R., Huang, D., Wan, J., Xue, W., Lei, L., Wen, X., Liu, X., Chen, S., Yang, Y., Li, Z., Li, B., 2019a. Chloro-phosphate impregnated biochar prepared by co-precipitation for the lead, cadmium and copper synergic scavenging from aqueous solution. Bioresour. Technol. 293, 122102.

Deng, R., Huang, D., Zeng, G., Wan, J., Xue, W., Wen, X., Liu, X., Chen, S., Li, J., Liu, C., 2019b. Decontamination of lead and tetracycline from aqueous solution by a promising carbonaceous nanocomposite: interaction and mechanisms insight. Bioresour. Technol. 283, 277−285.

Ding, Z., Hu, X., Wan, Y., Wang, S., Gao, B., 2016. Removal of lead, copper, cadmium, zinc, and nickel from aqueous solutions by alkali-modified biochar: batch and column tests. J. Ind. Eng. Chem. 33, 239−245.

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

El-Banna, M.F., Mosa, A., Gao, B., Yin, X., Ahmad, Z., Wang, H., 2018. Sorption of lead ions onto oxidized bagasse-biochar mitigates Pb-induced oxidative stress on hydroponically grown chicory: experimental observations and mechanisms. Chemosphere 208, 887−898.

El-Banna, M.F., Mosa, A., Gao, B., Yin, X., Wang, H., Ahmad, Z., 2019. Scavenging effect of oxidized biochar against the phytotoxicity of lead ions on hydroponically grown chicory: an anatomical and ultrastructural investigation. Ecotoxicol. Environ. Saf. 170, 363−374.

Fang, J., Gao, B., Mosa, A., Zhan, L., 2017. Chemical activation of hickory and peanut hull hydrochars for removal of lead and methylene blue from aqueous solutions. Chem. Speciat. Bioavailab. 29 (1), 197−204.

Fang, J., Zhan, L., Ok, Y.S., Gao, B., 2018. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. J. Ind. Eng. Chem. 57, 15−21.

Feng, Z., Zhu, L., 2018. Sorption of phenanthrene to biochar modified by base. Front. Environ. Sci. Eng. 12 (2), 1.

Foroutan, R., Mohammadi, R., Ramavandi, B., 2018. Treatment of chromium-laden aqueous solution using CaCl$_2$-modified Sargassum oligocystum biomass: characteristics, equilibrium, kinetic, and thermodynamic studies. Korean J. Chem. Eng. 35 (1), 234−245.

Gao, R., Fu, Q., Hu, H., Wang, Q., Liu, Y., Zhu, J., 2019. Highly-effective removal of Pb by co-pyrolysis biochar derived from rape straw and orthophosphate. J. Hazard Mater. 371, 191−197.

Hu, X., Ding, Z., Zimmerman, A.R., Wang, S., Gao, B., 2015. Batch and column sorption of arsenic onto iron-impregnated biochar synthesized through hydrolysis. Water Res. 68, 206−216.

Huang, D., Deng, R., Wan, J., Zeng, G., Xue, W., Wen, X., Zhou, C., Hu, L., Liu, X., Xu, P., Guo, X., Ren, X., 2018a. Remediation of lead-contaminated sediment by biochar-supported nano-chlorapatite: accompanied with the change of available phosphorus and organic matters. J. Hazard Mater. 348, 109−116.

Huang, D., Hu, Z., Peng, Z., Zeng, G., Chen, G., Zhang, C., Cheng, M., Wan, J., Wang, X., Qin, X., 2018b. Cadmium immobilization in river sediment using stabilized nanoscale zero-valent iron with enhanced transport by polysaccharide coating. J. Environ. Manag. 210, 191−200.

Huang, D., Liu, C., Zhang, C., Deng, R., Wang, R., Xue, W., Luo, H., Zeng, G., Zhang, Q., Guo, X., 2019a. Cr (VI) removal from aqueous solution using biochar modified with Mg/Al-layered double hydroxide intercalated with ethylenediaminetetraacetic acid. Bioresour. Technol. 276, 127−132.

Huang, D., Xue, W., Zeng, G., Wan, J., Chen, G., Huang, C., Zhang, C., Cheng, M., Xu, P., 2016. Immobilization of Cd in river sediments by sodium alginate modified

nanoscale zero-valent iron: impact on enzyme activities and microbial community diversity. Water Res. 106, 15–25.

Huang, Y., Xia, S., Lyu, J., Tang, J., 2019b. Highly efficient removal of aqueous Hg^{2+} and CH_3Hg^+ by selective modification of biochar with 3-mercaptopropyltrimethoxysilane. Chem. Eng. J. 360, 1646–1655.

Ifthikar, J., Jiao, X., Ngambia, A., Wang, T., Khan, A., Jawad, A., Xue, Q., Liu, L., Chen, Z., 2018. Facile one-pot synthesis of sustainable carboxymethyl chitosan–sewage sludge biochar for effective heavy metal chelation and regeneration. Bioresour. Technol. 262, 22–31.

Inyang, M.I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., Pullammanappallil, P., Ok, Y.S., Cao, X., 2016. A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. Crit. Rev. Biotechnol. 46 (4), 406–433.

Jiang, S., Huang, L., Nguyen, T.A., Ok, Y.S., Rudolph, V., Yang, H., Zhang, D., 2016. Copper and zinc adsorption by softwood and hardwood biochars under elevated sulphate-induced salinity and acidic pH conditions. Chemosphere 142, 64–71.

Jiang, X., Xiang, X., Hu, H., Meng, X., Hou, L., 2018. Facile fabrication of Biochar/Al_2O_3 adsorbent and its application for fluoride removal from aqueous solution. J. Chem. Eng. Data 64 (1), 83–89.

Jin, H., Hanif, M.U., Capareda, S., Chang, Z., Huang, H., Ai, Y., 2016. Copper (II) removal potential from aqueous solution by pyrolysis biochar derived from anaerobically digested algae-dairy-manure and effect of KOH activation. J. Environ. Chem. Eng. 4 (1), 365–372.

Jin, J., Li, S., Peng, X., Liu, W., Zhang, C., Yang, Y., Han, L., Du, Z., Sun, K., Wang, X., 2018. HNO_3 modified biochars for uranium (VI) removal from aqueous solution. Bioresour. Technol. 256, 247–253.

Kambo, H.S., Dutta, A., 2015. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. Renew. Sustain. Energy Rev. 45, 359–378.

Kobielska, P.A., Howarth, A.J., Farha, O.K., Nayak, S., 2018. Metal–organic frameworks for heavy metal removal from water. Coord. Chem. Rev. 358, 92–107.

Lau, A.Y., Tsang, D.C., Graham, N.J., Ok, Y.S., Yang, X., Li, X.-d., 2017. Surface-modified biochar in a bioretention system for Escherichia coli removal from stormwater. Chemosphere 169, 89–98.

Lei, C., Sun, Y., Tsang, D.C.W., Lin, D., 2018. Environmental transformations and ecological effects of iron-based nanoparticles. Environ. Pollut. 232, 10–30.

Li, B., Yang, L., Wang, C.Q., Zhang, Q.P., Liu, Q.C., Li, Y.D., Xiao, R., 2017. Adsorption of Cd (II) from aqueous solutions by rape straw biochar derived from different modification processes. Chemosphere 175, 332–340.

Li, R., Deng, H., Zhang, X., Wang, J.J., Awasthi, M.K., Wang, Q., Xiao, R., Zhou, B., Du, J., Zhang, Z., 2019. High-efficiency removal of Pb (II) and humate by a CeO_2–MoS_2 hybrid magnetic biochar. Bioresour. Technol. 273, 335–340.

Li, Y., Pei, G., Qiao, X., Zhu, Y., Li, H., 2018. Remediation of cadmium contaminated water and soil using vinegar residue biochar. Environ. Sci. Pollut. Res. 25, 15754–15764.

Li, Y., Shao, J., Wang, X., Deng, Y., Yang, H., Chen, H., 2014. Characterization of modified biochars derived from bamboo pyrolysis and their utilization for target component (furfural) adsorption. Energy Fuel. 28 (8), 5119–5127.

Liang, J., Li, X., Yu, Z., Zeng, G., Luo, Y., Jiang, L., Yang, Z., Qian, Y., Wu, H., 2017. Amorphous MnO_2 modified biochar derived from aerobically composted swine manure for adsorption of Pb (II) and Cd (II). ACS Sustain. Chem. Eng. 5 (6), 5049–5058.

Lin, L., Qiu, W., Wang, D., Huang, Q., Song, Z., Chau, H.W., 2017. Arsenic removal in aqueous solution by a novel Fe-Mn modified biochar composite: characterization and mechanism. Ecotoxicol. Environ. Saf. 144, 514–521.

Liu, T., Gao, B., Fang, J., Wang, B., Cao, X., 2016a. Biochar-supported carbon nanotube and graphene oxide nanocomposites for Pb (II) and Cd (II) removal. RSC Adv. 6 (29), 24314–24319.

Liu, W.J., Ling, L., Wang, Y.Y., He, H., He, Y.R., Yu, H.Q., Jiang, H., 2016b. One-pot high yield synthesis of Ag nanoparticle-embedded biochar hybrid materials from waste biomass for catalytic Cr (VI) reduction. Environ. Sci.: Nano 3 (4), 745–753.

Luo, M., Lin, H., He, Y., Li, B., Dong, Y., Wang, L., 2019. Efficient simultaneous removal of cadmium and arsenic in aqueous solution by titanium-modified ultrasonic biochar. Bioresour. Technol. 284, 333–339.

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

Melo, L.C., Coscione, A.R., Abreu, C.A., Puga, A.P., Camargo, O.A., 2013. Influence of pyrolysis temperature on cadmium and zinc sorption capacity of sugar cane straw–derived biochar. Bioresources 8 (4), 4992–5004.

Mohanty, S.K., Valenca, R., Berger, A.W., Yu, I.K.M., Xiong, X., Saunders, T.M., Tsang, D.C.W., 2018. Plenty of room for carbon on the ground: potential applications of biochar for stormwater treatment. Sci. Total Environ. 625, 1644–1658.

Niazi, N.K., Bibi, I., Shahid, M., Ok, Y.S., Burton, E.D., Wang, H., Shaheen, S.M., Rinklebe, J., Lüttge, A., 2018. Arsenic removal by perilla leaf biochar in aqueous solutions and groundwater: an integrated spectroscopic and microscopic examination. Environ. Pollut. 232, 31–41.

Palansooriya, K.N., Yang, Y., Tsang, Y.F., Sarkar, B., Hou, D., Cao, X., Meers, E., Rinklebe, J., Kim, K.H., Ok, Y.S., 2019. Occurrence of contaminants in drinking water sources and the potential of biochar for water quality improvement: a review. Crit. Rev. Environ. Sci. Technol. 1–63.

Park, J.H., Wang, J.J., Zhou, B., Mikhael, J.E., DeLaune, R.D., 2019. Removing mercury from aqueous solution using sulfurized biochar and associated mechanisms. Environ. Pollut. 244, 627–635.

Peng, H., Gao, P., Chu, G., Pan, B., Peng, J., Xing, B., 2017. Enhanced adsorption of Cu (II) and Cd (II) by phosphoric acid-modified biochars. Environ. Pollut. 229, 846–853.

Premarathna, K.S.D., Rajapaksha, A.U., Sarkar, B., Kwon, E.E., Bhatnagar, A., Ok, Y.S., Vithanage, M., 2019. Biochar-based engineered composites for sorptive decontamination of water: a review. Chem. Eng. J. 372, 536–550.

Rajapaksha, A.U., Alam, M.S., Chen, N., Alessi, D.S., Igalavithana, A.D., Tsang, D.C.W., Ok, Y.S., 2018. Removal of hexavalent chromium in aqueous solutions using biochar: chemical and spectroscopic investigations. Sci. Total Environ. 625, 1567–1573.

Rajapaksha, A.U., Chen, S.S., Tsang, D.C., Zhang, M., Vithanage, M., Mandal, S., Gao, B., Bolan, N.S., Ok, Y.S., 2016. Engineered/designer biochar for contaminant removal/immobilization from soil and water: potential and implication of biochar modification. Chemosphere 148, 276–291.

Rajapaksha, A.U., Vithanage, M., Ahmad, M., Seo, D.C., Cho, J.S., Lee, S.E., Lee, S.S., Ok, Y.S., 2015. Enhanced sulfamethazine removal by steam-activated invasive plant-derived biochar. J. Hazard Mater. 290, 43–50.

Ruan, X., Sun, Y., Du, W., Tang, Y., Liu, Q., Zhang, Z., Doherty, W., Frost, R.L., Qian, G., Tsang, D.C.W., 2019. Formation, characteristics, and applications of environmentally persistent free radicals in biochars: a review. Bioresour. Technol. 281, 457–468.

Shaheen, S.M., Niazi, N.K., Hassan, N.E.E., Bibi, I., Wang, H., Tsang, Daniel C.W., Ok, Y.S., Bolan, N., Rinklebe, J., 2018. Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review. Int. Mater. Rev. 64 (4), 216–247.

Shang, M.R., Liu, Y.G., Liu, S.B., Zeng, G.M., Tan, X.F., Jiang, L.H., Huang, X.X., Ding, Y., Guo, Y.M., Wang, S.F., 2016. A novel graphene oxide coated biochar composite: synthesis, characterization and application for Cr (VI) removal. RSC Adv. 6 (88), 85202–85212.

Shen, Z., Hou, D., Jin, F., Shi, J., Fan, X., Tsang, D.C.W., Alessi, D.S., 2019. Effect of production temperature on lead removal mechanisms by rice straw biochars. Sci. Total Environ. 655, 751–758.

Shi, J., Fan, X., Tsang, D.C.W., Wang, F., Shen, Z., Hou, D., Alessi, D.S., 2019. Removal of lead by rice husk biochars produced at different temperatures and implications for their environmental utilizations. Chemosphere 235, 825–831.

Shi, S., Yang, J., Liang, S., Li, M., Gan, Q., Xiao, K., Hu, J., 2018. Enhanced Cr (VI) removal from acidic solutions using biochar modified by Fe_3O_4@ SiO_2-NH_2 particles. Sci. Total Environ. 628, 499–508.

Sizmur, T., Fresno, T., Akgül, G., Frost, H., Moreno-Jiménez, E., 2017. Biochar modification to enhance sorption of inorganics from water. Bioresour. Technol. 246, 34–47.

Song, J., He, Q., Hu, X., Zhang, W., Wang, C., Chen, R., Wang, H., Mosa, A., 2019. Highly efficient removal of Cr(VI) and Cu(II) by biochar derived from Artemisia argyi stem. Environ. Sci. Pollut. Res. 26, 13221–13234.

Sun, K., Tang, J., Gong, Y., Zhang, H., 2015a. Characterization of potassium hydroxide (KOH) modified hydrochars from different feedstocks for enhanced removal of heavy metals from water. Environ. Sci. Pollut. Res. 22, 16640–16651.

Sun, L., Chen, D., Wan, S., Yu, Z., 2015b. Performance, kinetics, and equilibrium of methylene blue adsorption on biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids. Bioresour. Technol. 198, 300–308.

Sun, P., Li, Y., Meng, T., Zhang, R., Song, M., Ren, J., 2018. Removal of sulfonamide antibiotics and human metabolite by biochar and biochar/H_2O_2 in synthetic urine. Water Res. 147, 91–100.

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

Tan, G., Sun, W., Xu, Y., Wang, H., Xu, N., 2016a. Sorption of mercury (II) and atrazine by biochar, modified biochars and biochar based activated carbon in aqueous solution. Bioresour. Technol. 211, 727–735.

Tan, X.F., Liu, Y.G., Gu, Y.L., Xu, Y., Zeng, G.M., Hu, X.J., Liu, S.B., Wang, X., Liu, S.M., Li, J., 2016b. Biochar-based nano-composites for the decontamination of wastewater: a review. Bioresour. Technol. 212, 318–333.

Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere 125, 70–85.

Tan, Z., Wang, Y., Kasiulienė, A., Huang, C., Ai, P., 2017a. Cadmium removal potential by rice straw-derived magnetic biochar. Clean Technol. Environ. Policy 19 (3), 761–774.

Tan, Z., Wang, Y., Zhang, L., Huang, Q., 2017b. Study of the mechanism of remediation of Cd-contaminated soil by novel biochars. Environ. Sci. Pollut. Res. 24, 24844–24855.

Tang, J., Lv, H., Gong, Y., Huang, Y., 2015. Preparation and characterization of a novel graphene/biochar composite for aqueous phenanthrene and mercury removal. Bioresour. Technol. 196, 355–363.

Trakal, L., Veselská, V., Šafařík, I., Vítková, M., Číhalová, S., Komárek, M., 2016. Lead and cadmium sorption mechanisms on magnetically modified biochars. Bioresour. Technol. 203, 318–324.

Uchimiya, M., Hiradate, S., Antal, M.J., 2015. Dissolved phosphorus speciation of flash Carbonization, slow Pyrolysis, and fast pyrolysis biochars. Acs Sustain. Chem. Eng. 3 (7), 1642–1649.

Wan, J., Zeng, G., Huang, D., Hu, L., Xu, P., Huang, C., Deng, R., Xue, W., Lai, C., Zhou, C., Zheng, K., Ren, X., Gong, X., 2018. Rhamnolipid stabilized nano-chlorapatite: synthesis and enhancement effect on Pb-and Cd-immobilization

in polluted sediment. J. Hazard Mater. 343, 332—339.

Wan, Z., Cho, D.W., Tsang, D.C.W., Li, M., Sun, T., Verpoort, F., 2019. Concurrent adsorption and micro-electrolysis of Cr(VI) by nanoscale zerovalent iron/biochar/Ca-alginate composite. Environ. Pollut. 247, 410—420.

Wang, B., Gao, B., Fang, J., 2018a. Recent advances in engineered biochar productions and applications. Crit. Rev. Environ. Sci. Technol. 47 (22), 2158—2207.

Wang, H., Gao, B., Wang, S., Fang, J., Xue, Y., Yang, K., 2015. Removal of Pb (II), Cu (II), and Cd (II) from aqueous solutions by biochar derived from KMnO4 treated hickory wood. Bioresour. Technol. 197, 356—362.

Wang, J., Wang, S., 2019. Preparation, modification and environmental application of biochar: a review. J. Clean. Prod. 227, 1002—1022.

Wang, R.Z., Huang, D.L., Liu, Y.G., Zhang, C., Lai, C., Zeng, G.M., Cheng, M., Gong, X.M., Wan, J., Luo, H., 2018b. Investigating the adsorption behavior and the relative distribution of Cd^{2+} sorption mechanisms on biochars by different feedstock. Bioresour. Technol. 261, 265—271.

Wang, S., Zhao, M., Zhou, M., Li, Y.C., Wang, J., Gao, B., Sato, S., Feng, K., Yin, W., Igalavithana, A.D., Oleszczuk, P., Wang, X., Ok, Y.S., 2019. Biochar-supported nZVI (nZVI/BC) for contaminant removal from soil and water: a critical review. J. Hazard Mater. 373, 820—834.

Wang, T., Liu, J., Zhang, Y., Zhang, H., Chen, W.Y., Norris, P., Pan, W.P., 2018c. Use of a non-thermal plasma technique to increase the number of chlorine active sites on biochar for improved mercury removal. Chem. Eng. J. 331, 536—544.

Wang, T., Wu, J., Zhang, Y., Liu, J., Sui, Z., Zhang, H., Chen, W.Y., Norris, P., Pan, W.P., 2018d. Increasing the chlorine active sites in the micropores of biochar for improved mercury adsorption. Fuel 229, 60—67.

Wongrod, S., Simon, S., Guibaud, G., Lens, P.N., Pechaud, Y., Huguenot, D., van Hullebusch, E.D., 2018. Lead sorption by biochar produced from digestates: consequences of chemical modification and washing. J. Environ. Manag. 219, 277—284.

Wu, J., Huang, D., Liu, X., Meng, J., Tang, C., Xu, J., 2018. Remediation of as (III) and Cd (II) co-contamination and its mechanism in aqueous systems by a novel calcium-based magnetic biochar. J. Hazard Mater. 348, 10—19.

Xia, D., Tan, F., Zhang, C., Jiang, X., Chen, Z., Li, H., Zheng, Y., Li, Q., Wang, Y., 2016. ZnCl2-activated biochar from biogas residue facilitates aqueous as (III) removal. Appl. Surf. Sci. 377, 361—369.

Xu, X., Huang, H., Zhang, Y., Xu, Z., Cao, X., 2019a. Biochar as both electron donor and electron shuttle for the reduction transformation of Cr (VI) during its sorption. Environ. Pollut. 244, 423—430.

Xu, X., Schierz, A., Xu, N., Cao, X., 2016. Comparison of the characteristics and mechanisms of Hg (II) sorption by biochars and activated carbon. J. colloid and Interf. Sci. 463, 55—60.

Xu, Z., Chen, T., Ding, Z., Hu, X., Nie, G., 2019b. Effects of magnesium impregnation on stability and sorption performance of biochar derived from sawdust and corn husks. Bioresources 14 (1), 289—301.

Xu, Z., Xu, X., Tao, X., Yao, C., Tsang, D.C.W., Cao, X., 2019c. Interaction with low molecular weight organic acids affects the electron shuttling of biochar for Cr(VI) reduction. J. Hazard Mater. 378, 120705.

Xue, Y., Gao, B., Yao, Y., Inyang, M., Zhang, M., Zimmerman, A.R., Ro, K.S., 2012. Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: batch and column tests. Chem. Eng. J. 200, 673—680.

Yang, F., Zhang, S., Sun, Y., Cheng, K., Li, J., Tsang, D.C.W., 2018. Fabrication and characterization of hydrophilic corn stalk biochar-supported nanoscale zerovalent iron composites for efficient metal removal. Bioresour. Technol. 265, 490—497.

Yang, F., Zhang, S., Sun, Y., Du, Q., Song, J., Tsang, D.C.W., 2019a. A novel electrochemical modification combined with one-step pyrolysis for preparation of sustainable thorn-like iron-based biochar composites. Bioresour. Technol. 274, 379—385.

Yang, G.X., Jiang, H., 2014. Amino modification of biochar for enhanced adsorption of copper ions from synthetic wastewater. Water Res. 48, 396—405.

Yang, X., Ng, W., Wong, B.S.E., Baeg, G.H., Wang, C.H., Ok, Y.S., 2019b. Characterization and ecotoxicological investigation of biochar produced via slow pyrolysis: effect of feedstock composition and pyrolysis conditions. J. Hazard Mater. 365, 178—185.

You, S., Ok, Y.S., Tsang, D.C.W., Kwon, E.E., Wang, C.H., 2018. Towards practical application of gasification: a critical review from syngas and biochar perspectives. Crit. Rev. Environ. Sci. Technol. 4 (22—24), 1165—1213, 8.

Yu, J., Jiang, C., Guan, Q., Ning, P., Gu, J., Chen, Q., Zhang, J., Miao, R., 2018a. Enhanced removal of Cr (VI) from aqueous solution by supported ZnO nanoparticles on biochar derived from waste water hyacinth. Chemosphere 195, 632—640.

Yu, W., Lian, F., Cui, G., Liu, Z., 2018b. N-doping effectively enhances the adsorption capacity of biochar for heavy metal ions from aqueous solution. Chemosphere 193, 8—16.

Zamani, S.A., Yunus, R., Samsuri, A., Salleh, M., Asady, B., 2017. Removal of Zinc from aqueous solution by optimized oil palm empty Fruit bunches biochar as low cost adsorbent. Bioinorgan. Chem. Appl. 7914714.

Zeng, Z., Ye, S., Wu, H., Xiao, R., Zeng, G., Liang, J., Zhang, C., Yu, J., Fang, Y., Song, B., 2019. Research on the sustainable efficacy of g-MoS2 decorated biochar nanocomposites for removing tetracycline hydrochloride from antibiotic-polluted aqueous solution. Sci. Total Environ. 648, 206—217.

Zhang, M.M., Liu, Y.G., Li, T.T., Xu, W.H., Zheng, B.H., Tan, X.F., Wang, H., Guo, Y.M., Guo, F.F., Wang, S.F., 2015. Chitosan modification of magnetic biochar produced from Eichhornia crassipes for enhanced sorption of Cr (VI) from aqueous solution. RSC Adv. 5 (58), 46955—46964.

Zhang, W., Wang, H., Hu, X., Feng, H., Xiong, W., Guo, W., Zhou, J., Mosa, A., Peng, Y., 2019. Multicavity triethylenetetramine-chitosan/alginate composite beads for enhanced Cr(VI) removal. J. Clean. Prod. 231, 733—745.

Zhao, N., Yin, Z., Liu, F., Zhang, M., Lv, Y., Hao, Z., Pan, G., Zhang, J., 2018. Environmentally persistent free radicals mediated removal of Cr (VI) from highly saline water by corn straw biochars. Bioresour. Technol. 260, 294—301.

Zhou, Y., Gao, B., Zimmerman, A.R., Fang, J., Sun, Y., Cao, X., 2013. Sorption of heavy metals on chitosan-modified biochars and its biological effects. Chem. Eng. J. 231, 512—518.

Zhou, Z., Liu, Y.G., Liu, S.B., Liu, H.Y., Zeng, G.M., Tan, X.F., Yang, C.P., Ding, Y., Yan, Z.L., Cai, X.X., 2017. Sorption performance and mechanisms of arsenic (V) removal by magnetic gelatin-modified biochar. Chem. Eng. J. 314, 223—231.

Zhu, S., Ho, S.H., Huang, X., Wang, D., Yang, F., Wang, L., Wang, C., Cao, X., Ma, F., 2017. Magnetic nanoscale zerovalent iron assisted biochar: interfacial chemical behaviors and heavy metals remediation performance. Acs Sustain. Chem. Eng. 5 (11), 9673—9682.