Review on utilization of biochar for metal-contaminated soil and sediment remediation

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ABSTRACT

Biochar is a carbon-neutral or even carbon-negative material produced through thermal decomposition of plant- and animal-based biomass under oxygen-limited conditions. Recently, there has been an increasing interest in the application of biochar as an adsorbent, soil ameliorant and climate mitigation approach in many types of applications. Metal-contaminated soil remediation using biochar has been intensively investigated in small-scale and pilot-scale trials with obtained beneficial results and multifaceted effects. But so far, the study and application of biochar in contaminated sediment management has been very limited, and this is also a worldwide problem. Nonetheless, there is reason to believe that the same multiple benefits can also be realized with these sediments due to similar mechanisms for stabilizing contaminants. This paper provides a review on current biochar properties and its use as a sorbent/amendment for metal-contaminated soil/sediment remediation and its effect on plant growth, fauna habits as well as microorganism communities. In addition, the use of biochar as a potential strategy for contaminated sediment management is also discussed, especially as regards in-situ planning. Finally, we highlight the possibility of biochar application as an effective amendment and propose further research directions to ensure the safe and sustainable use of biochar as an amendment for remediation of contaminated soil and sediment.

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Introduction

Soil and sediment contamination by heavy metals

Due to some detrimental properties of heavy metals including mobility, non-decomposed, bioaccumulation and ecotoxicity, soil and sediments contaminated by metals have attracted much attention from concerned authorities (Bolan et al., 2014; Bastami et al., 2015), since they can pose a critical threat to the soil and aquatic environments. In recent years, high concentrations of metals such as As, Cd, Cu, Pb, and Zn in soils and sediments have often been reported in a number of countries. For example, significant negative impacts of metal pollutants on human health have been recorded in Bangladesh, India and China, and it is claimed that millions of people are potentially at risk from metal contamination (Ranadhar et al., 2012; Bolan et al., 2014). In several cities of China, nearly all the measured concentrations of metals in urban soils, urban road dusts and agricultural soils are higher than their background values (Wei and Yang, 2010). Likewise, the situation in the aquatic benthic environment is also less than optimistic (Akcil et al., 2015; Yang et al., 2016; Zhang et al., 2016).

In terrestrial systems, soil is the major repository of chemical contaminants. The basic material requirements of human beings also largely depend on the yield of land farming and management for survival and development. Metals retained in the soil by sorption, precipitation and complexation can undergo a series of processes such as plant uptake, leaching, volatilization, redox and (de)methylation (Boening, 2000; Porter and Scheckel, 2004; Lu et al., 2011). Because the residence of these pollutants in the soil is almost permanent and they cannot be disintegrated through organic activity, they not only can lead to crop yield and quality problems, but can also endanger the health of human beings and animals through direct exposure and the food chain (Adriano et al., 2004; Park et al., 2011a; Bolan et al., 2014).

In aquatic ecosystems, sediments are the major sink and source of pollutants and they play an important role in both the environment and ecology (Zhang et al., 2014). Once metals enter an aquatic system, almost 90% of these pollutants deposit onto sediment surfaces (Zhang and Shan, 2008; Amin et al., 2009) as result of adsorption, precipitation, flocculation and incorporation into the lattice structures of minerals (Akcil et al., 2015; Laing et al., 2009; Lin et al., 2013). However, if the benthic and water environmental parameters change, bound metals can be released from sediments to become more mobile and bioavailable (Westerlund and Viklander, 2006; Atkinson et al., 2007).

Thus, it is important to improve contaminants’ stability and reduce their bioavailability and migration ability in natural matrices. Conventional management or remediation methods for soil and sediments can involve in- and/or ex-situ planning (Akcil et al., 2015). In fact, many treatment strategies proposed for the remediation of metal-contaminated sediments stem from techniques developed for soil management (Akcil et al., 2015). Once sediments are dredged from aquatic benthic environments and subjected to pretreatment such as dehydration, the subsequent treatment planning is very close to that for soil remediation (Fig. 1), including washing, thermal treatment, electrolytic processes, solidification/stabilization and so on (Mulligan et al., 2001; Gomes et al., 2013). The main aim of those actions is reducing the concentration of contaminants and decreasing their properties of mobility and bioavailability; the interaction between metal characteristics and their bioavailability is shown in Fig. 2 (Bolan et al., 2014). Nevertheless, the conditions for in-situ treatments may be different between soil and sediment, because the processes of contaminant transport and their geochemical behaviors can be more complicated in aquatic benthic conditions than in soil. The limitation of using soil remediation strategies on sediment management is the efficiency and feasibility of procedures conducted in benthic conditions. However, studies and applications can still learn from the methods and techniques developed from soil management.

As an alternative approach, sorbent amendments and stabilization strategies can strengthen contaminant binding both in ex- and in-situ remediation, likely promoting biogeochemical processes and potentially reducing ecological risks (Cornelissen et al., 2005; Millward et al., 2005). Several mineral-based materials have already been studied to remedy
metal-contaminated soils and sediments, such as zero-valent iron, hematite, ferrihydrite, apatite and clays (Qian et al., 2009; Su et al., 2016). Yin and Zhu (2016) investigated the natural calcium-rich clay minerals sepiolite and attapulgite to remediate Pb- and Cd-polluted sediment, and their results showed that these amendments can effectively reduce both the mobile metal fraction and the bioavailability to benthic organisms, with more positive results at increased dose. Moreover, black carbons, such as activated carbon and biochar, have also exhibited excellent properties as amendments (Ghosh et al., 2011; Denyes et al., 2013) in contaminated site remediation, and these applications have attracted much attention in recent years. However, in prior studies activated carbon has been investigated and utilized frequently in many aspects (Cho et al., 2007; Hilber and Bucheli, 2010; Choi et al., 2016), while biochar was not as widely recognized and systematically studied until the year 2006 (Mitchell, 2007).

Biochar application for environmental management

Biochar is obtained from the thermochemical conversion of biomass in an oxygen-limited condition (International Biochar Initiative, 2012). Some common definitions of the product are “the porous carbonaceous solid produced by the thermochemical conversion of organic materials in an oxygen depleted atmosphere that has physicochemical properties…"
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<th>Ash (%)</th>
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<td>0.15</td>
<td>0.02</td>
<td>0.087</td>
<td>0.115</td>
<td>54.05</td>
<td>0.0894</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(Zielińska, 2016)</td>
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<tr>
<td>KZ sludge 500</td>
<td>– – –</td>
<td>23.2 0.7</td>
<td>4.42 3.5</td>
<td>0.39</td>
<td>0.14</td>
<td>0.132</td>
<td>0.275</td>
<td>16.28</td>
<td>0.0326</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(Zielińska, 2016)</td>
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<tr>
<td>KZ sludge 600</td>
<td>– – –</td>
<td>23.7 0.4</td>
<td>2.29 3.2</td>
<td>0.22</td>
<td>0.07</td>
<td>0.119</td>
<td>0.191</td>
<td>8.99</td>
<td>0.0295</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(Zielińska, 2016)</td>
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<tr>
<td>KZ sludge 700</td>
<td>– – –</td>
<td>22.8 0.3</td>
<td>0.3 2.2</td>
<td>0.17</td>
<td>0.01</td>
<td>0.084</td>
<td>0.094</td>
<td>29.87</td>
<td>0.0489</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(Zielińska, 2016)</td>
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<tr>
<td>CM sludge 500</td>
<td>– – –</td>
<td>22.4 0.6</td>
<td>4.94 3.0</td>
<td>0.35</td>
<td>0.16</td>
<td>0.115</td>
<td>0.280</td>
<td>34.15</td>
<td>0.0483</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(Zielińska, 2016)</td>
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<tr>
<td>CM sludge 600</td>
<td>– – –</td>
<td>22.4 0.6</td>
<td>4.09 2.6</td>
<td>0.33</td>
<td>0.13</td>
<td>0.102</td>
<td>0.238</td>
<td>16.4</td>
<td>0.0422</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(Zielińska, 2016)</td>
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<tr>
<td>CM sludge 700</td>
<td>– – –</td>
<td>21.7 0.56</td>
<td>3.34 2.4</td>
<td>0.31</td>
<td>0.11</td>
<td>0.095</td>
<td>0.210</td>
<td>9.22</td>
<td>0.0321</td>
<td>–</td>
<td>–</td>
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<td>(Zielińska, 2016)</td>
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<tr>
<td>SI sludge 500</td>
<td>– – –</td>
<td>26.6 1.0</td>
<td>4.29 3.9</td>
<td>0.48</td>
<td>0.12</td>
<td>0.127</td>
<td>0.248</td>
<td>35.66</td>
<td>0.0633</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(Zielińska, 2016)</td>
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<tr>
<td>SI sludge 600</td>
<td>– – –</td>
<td>27.7 0.8</td>
<td>3.89 3.7</td>
<td>0.35</td>
<td>0.10</td>
<td>0.116</td>
<td>0.222</td>
<td>19.15</td>
<td>0.0495</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(Zielińska, 2016)</td>
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<tr>
<td>SI sludge 700</td>
<td>– – –</td>
<td>27.8 0.4</td>
<td>0.79 2.9</td>
<td>0.20</td>
<td>0.02</td>
<td>0.090</td>
<td>0.111</td>
<td>18.13</td>
<td>0.0535</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(Zielińska, 2016)</td>
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<tr>
<td>Bamboo reed 300</td>
<td>44.4 7.7 8.4</td>
<td>65.3 4.5</td>
<td>21 0.65</td>
<td>0.82</td>
<td>0.24</td>
<td>0.009</td>
<td>0.250</td>
<td>2.72</td>
<td>–</td>
<td>2.69</td>
<td>–</td>
<td>(Zheng, 2013)</td>
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<tr>
<td>Bamboo reed 350</td>
<td>41.7 7.7 8.1</td>
<td>67 4.4</td>
<td>21.7 0.64</td>
<td>0.79</td>
<td>0.21</td>
<td>0.008</td>
<td>0.251</td>
<td>2.16</td>
<td>–</td>
<td>2.27</td>
<td>–</td>
<td>(Zheng, 2013)</td>
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<tr>
<td>Bamboo reed 400</td>
<td>40 8.5 8.1</td>
<td>72.3 4.0</td>
<td>18.7 0.67</td>
<td>0.67</td>
<td>0.19</td>
<td>0.008</td>
<td>0.202</td>
<td>3.04</td>
<td>–</td>
<td>1.75</td>
<td>–</td>
<td>(Zheng, 2013)</td>
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<tr>
<td>Bamboo reed 500</td>
<td>33.4 10.7 9.7</td>
<td>73.1 3.0</td>
<td>11.5 0.63</td>
<td>0.49</td>
<td>0.12</td>
<td>0.007</td>
<td>0.125</td>
<td>2.58</td>
<td>–</td>
<td>1.16</td>
<td>–</td>
<td>(Zheng, 2013)</td>
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<tr>
<td>Bamboo reed 600</td>
<td>30.6 11.3 10.7</td>
<td>78.6 2.2</td>
<td>11.2 0.55</td>
<td>0.33</td>
<td>0.10</td>
<td>0.006</td>
<td>0.113</td>
<td>50.0</td>
<td>–</td>
<td>0.98</td>
<td>–</td>
<td>(Zheng, 2013)</td>
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<tr>
<td>Bagasse 350</td>
<td>52.27 6.0 5.7</td>
<td>73.1 1.7</td>
<td>2.4 0.28</td>
<td>0.029</td>
<td>–</td>
<td>110.52</td>
<td>0.145</td>
<td>4.126</td>
<td>0.438</td>
<td>Liu, 2014</td>
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<tr>
<td>Bagasse 450</td>
<td>22.28 6.45 6.4</td>
<td>68.9 1.4</td>
<td>2.3 0.24</td>
<td>0.029</td>
<td>–</td>
<td>160.36</td>
<td>0.191</td>
<td>2.604</td>
<td>0.555</td>
<td>Liu, 2014</td>
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<tr>
<td>Bagasse 550</td>
<td>18.2 8.0 8.9</td>
<td>84.8 1.4</td>
<td>2.2 0.19</td>
<td>0.022</td>
<td>–</td>
<td>298.4</td>
<td>0.77</td>
<td>1.442</td>
<td>0.856</td>
<td>Liu, 2014</td>
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<tr>
<td>Bagasse 650</td>
<td>17.47 8.0 9.1</td>
<td>82.7 1.2</td>
<td>2.0 0.17</td>
<td>0.021</td>
<td>–</td>
<td>483.43</td>
<td>0.839</td>
<td>0.982</td>
<td>1.253</td>
<td>Liu, 2014</td>
<td></td>
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<tr>
<td>Bagasse 750</td>
<td>16.79 8.1 9.4</td>
<td>82.9 1.1</td>
<td>1.9 0.16</td>
<td>0.020</td>
<td>–</td>
<td>620.05</td>
<td>0.94</td>
<td>0.536</td>
<td>1.425</td>
<td>Liu, 2014</td>
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<tr>
<td>Cassava residue 350</td>
<td>29.8 12.8 6.0</td>
<td>58.5 3.57</td>
<td>1.5 0.73</td>
<td>0.022</td>
<td>–</td>
<td>48.19</td>
<td>0.08</td>
<td>1.746</td>
<td>1.541</td>
<td>Liu, 2014</td>
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<tr>
<td>Cassava residue 450</td>
<td>29.64 16.4 7.2</td>
<td>63.6 3.2</td>
<td>1.3 0.60</td>
<td>0.018</td>
<td>–</td>
<td>80.56</td>
<td>0.135</td>
<td>0.988</td>
<td>1.653</td>
<td>Liu, 2014</td>
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<tr>
<td>Cassava residue 550</td>
<td>23.61 17.1 7.4</td>
<td>68.9 2.4</td>
<td>1.2 0.42</td>
<td>0.016</td>
<td>–</td>
<td>167.55</td>
<td>0.183</td>
<td>0.71</td>
<td>1.846</td>
<td>Liu, 2014</td>
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<tr>
<td>Cassava residue 650</td>
<td>21.55 23.4 9.3</td>
<td>70.4 1.8</td>
<td>1.2 0.31</td>
<td>0.015</td>
<td>–</td>
<td>291.76</td>
<td>0.155</td>
<td>0.533</td>
<td>2.335</td>
<td>Liu, 2014</td>
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suitable for safe and long-term storage of carbon in the environment" (Shackley et al., 2012) and "biomass that has been pyrolyzed in a zero or low oxygen environment applied to soil at a specific site that is expected to sustainably sequester C and concurrently improve soil functions under current and future management, while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health" (Verheijen et al., 2010). Those definitions focus on the conditions and procedures of producing biochar and its application for soil amelioration and to mitigate climate change. According to our understanding, biochar is produced via thermal decomposition of biomass, including agricultural waste, plants and husks, fermentation residue and poultry manure, under oxygen limitations, and the produced biochar’s physical and chemical characteristics will differ based on the pyrolysis temperature and the feedstock, with intended use as an environmental amendment and soil modifier.

Currently it is becoming more common to use biochar as a soil amendment, with such an amelioration making for a “multiple-win” for contaminated soil and sediment, referring to carbon sequestration, soil fertility improvement, agronomic benefits, biofuel/bioenergy production, pollutant immobilization and waste disposal (Jeffery et al., 2015). Like activated carbon, biochar has the capability to adsorb and immobilize metal pollutants. In a prior leaching experiment, biochar manufactured from broiler litter was compared to activated carbon obtained from pecan shells for immobilizing and binding Cu, Ni and Cd. The biochar performed more effectively than activated carbon, especially for Cu (Uchimiya et al., 2010a). Similarly, bagasse and hickory chip-derived biochar was found to remove more Hg(II) in aqueous solution (about 13 and 5 mg/g, respectively) than coconut shell-derived activated carbon (about 3 mg/g) (Xu et al., 2016a). These results suggest that the functional sites of biochar are more diverse and numerous than activated carbon (AC) despite its lower surface area, and this may contribute to the ability of biochar to bind and sequester pollutants. Due to the incomplete carbonization of biochar as compared to AC, biochar consists of different proportions of carbonized and amorphous organic matter, so the properties of the biochar are closer to those of natural soil or sediment organic matter (Chun et al., 2004).

Furthermore, soil physicochemical properties can be improved by biochar application via the following aspects: (1) biochar is always alkaline (pH > 7), and obvious amelioration can be observed following biochar amendment in acid and neutral soils (Major et al., 2010) resulting in increased pH, although applications and effects in alkaline soils are more complicated since some alkaline reactions may occur (Gunes et al., 2014); (2) biochar can hold moisture, with the porous structure contributing to increasing the soil water holding capacity (Atkinson et al., 2010). In the Amazon, the anthrosol water holding rate was 18% higher than an adjacent soil without biochar, but in loamy soil no change was observed (Glaser et al., 2002); and (3) biochar can retain nutrients, preventing those substances from leaching and enhancing their uptake efficiency. In a field trial, during 4 years of biochar application, the nutrient uptake rate was 0.77–3.3-fold higher as compared to an unamended site (Major et al., 2010). However, some researchers have suggested that the bioavailability of the nutrients may also decrease after biochar application; for example sugar beet-derived biochar has been shown to adsorb phosphate strongly (Yao et al., 2011) and, in bare sites, this enhanced nutrient retention may reduce the possibility of revegetation (Beesley et al., 2011). Other suggested improvements from biochar amendments include soil texture, density, and porosity (Atkinson et al., 2010), consequently increasing the volume of crop output (Jeffery et al., 2011). Given all these multiple-win effects, in China, biochar already has been used as an ameliorant and amendment for remediation of metal-contaminated rice fields; a series of field trials and demonstration plots has been conducted in Guangxi, Fujian, Hunan, Jiangxi, Sichuan and Jiangsu provinces and obtained positive results with biochar application, decreasing metal bioavailability in soil by 20%–70% and reducing metal concentration in rice grains by 20%–60% (Pan and Li, 2013; Huang et al., 2013).

According to the results summarized here, biochar is a beneficial amendment in soil management and has already been widely studied and used in this field. Based on this, we can speculate that similar multifaceted benefits may also be realized for biochar amendments in contaminated sediment, and this speculation already has been borne out by some recent studies (Ojdeda et al., 2016; Chen et al., 2016; Liu et al., 2017). Similarly, contaminated sediment management also refers to not only the mobility and changes in concentration/total amount of pollutants, but also their bioavailability and fractionation (Chapman et al., 1998; Simpson et al., 2012), so that the ecological influence and all-around efficiency of the amendments should be fully considered.

In this paper, we aim to provide an overview of the following: (1) the characteristics of biochar, (2) the effect of biochar on metal mobility and stability, and (3) the biological effect and ecological remediation brought about by biochar application. According to these findings, using biochar as a potential amendment to remedy metals contaminated sediment is proposed, especially as an in-situ capping strategy. Finally, we also identify immediate research needs and suggest future directions for research.

### 1. Manufacture and characteristics of biochar

Studies have shown that the feedstock sources and heat treatment temperatures are major factors determining the physiochemical properties of biochar, as summarized in Table 1.

#### 1.1. Effects of biomass pyrolysis

It has been suggested that the carbon becomes less reactive and forms stable chemical structures as pyrolysis progresses (Demirbas, 2004a). Moreover, the biochar characteristics and byproducts depend on the heating rate, while the surface properties and pore structure rely on the heating temperature (Table 1) (Sohi et al., 2010).

Commonly, pyrolysis is classified as fast, intermediate and slow pyrolysis. Fast pyrolysis means shorter residence times and higher bio-oil yield (above 75%). Intermediate and slow
Pyrolysis may have heating ranges from several minutes to hours and the biochar yield is relatively low (25% and 35%, respectively) (Ahmad et al., 2014). Table 1 shows the various biochar properties and the significant parameters controlled by pyrolysis temperature, with the component content of biochar varying as the pyrolysis temperature increases. Pyrolysis is generally comprised of three stages, including pre-pyrolysis, main-pyrolysis and formation of a carbon-rich solid (Demirbas, 2004a). In the first stage, the temperature is below 200 °C and the internal structure is rearranged as related to moisture evaporation, bond breakage and formation of hydroperoxide, carboxyl and carbonyl groups. The second stage is the primary process where biomass decomposition occurs and the primary pyrolysis product is produced at a fast rate. In the final stage, the residual char is then further pyrolyzed and forms the biochar.

During the manufacturing process, several chemical additives (such as AlCl₃, FeCl₃, H₃PO₄, NH₄Cl, KOH and ZnCl₂) can inhibit hemicellulose decomposition but accelerate cellulose decomposition, and result in decomposition overlap (Demirbas, 2004b), which may affect the biochar yield and components. As temperature increases the biochar yield decreases; it was observed that at ≤400 °C the biochar yield was rapidly decreased, while a steady yield was observed at ≥400 °C (Ahmad et al., 2014). As for the biochar elemental composition, the carbon content increased with temperature, and opposite and variable relationships were observed for H, O and N (Table 1). The decrease of the H/C ratio represents the carbonization and increasing aromaticity of biochar, and a lower O/C and (O + N)/C ratio reflects a lower polarity of biochar (Chen and Chen, 2009). Thus, biochar obtained at lower temperatures with lower aromaticity consisted mainly of lignin and cellulose, whereas, biochar produced at higher temperatures was rich in aromatic moieties with lower polarity (Keiluweit et al., 2010; Uchimiya et al., 2010b). These results were further supported by Sun et al. (2011) who used 13C nuclear magnetic resonance (NMR) spectra to identify biochar aromaticity. In addition, through Fourier Transform infrared spectroscopy (FT-IR) analysis, some researchers found that the organic and inorganic functional groups were predominated by –OH, ester C=O, aromatic C=C, C–O and Si–O–Si at low temperatures (Qian et al., 2016), while as the temperature was increased, the organic functional groups were either decreased or eliminated, and new bonds were built as shown by the C=C aromatic stretching intensity (Eusterhues et al., 2010; Oren and Chefetz, 2012; Qian et al., 2016).

1.2. Effects of feedstock type

Carbon materials such as activated carbon and biochar can be manufactured from almost any carbonaceous material, including wood, coal, fruit shells, manure, fermentation and farming residuals and wastes from food, sugar and juice processing (Suliman et al., 2016). These biomass types contain various components and amounts of organic matter (such as hemicellulose, cellulose, lignin, fats, phytosterols and phenolics) and inorganic compounds (nitrogen, phosphorous, sulfur, silicon, alkali and alkaline earth metals, and various trace minerals) (McKendry, 2002), which can affect the final structure and properties of the produced biochar. As pointed out in the prior discussion, the content of C increases with temperature for most feedstocks, while the yield of biochar and the molar ratios of H/C and O/C decrease (Table 1). However, some studies reported that the C content of sewage sludge-obtained biochar decreased as temperature increased, but the H/C and (O+N)/C molar ratios still decreased with temperature rise in the same way as for the other feedstocks (Lu et al., 2013; Zielińska and Oleszczuk, 2016).

Generally, higher pyrolysis temperatures result in greater surface areas, therefore biochars possessing lower surface areas and pore volumes at higher temperatures may result from formation of extensive cross-linkages, cracking or blockage of the micropores with those feedstocks containing less volatile matter (Bourke et al., 2007; Liu et al., 2010). Besides being affected by heating temperature, higher biochar yield can also be obtained from lignin-rich and mineral-rich raw materials (Antal and Grønli, 2003; Collison et al., 2009). With respect to metals/metalloids, their concentrations and composition in produced biochar were more strongly influenced by the feedstocks rather than the heating temperature. Metals or metalloids showed higher concentrations in manure-derived biochar, and this may be related to food intake and bioaccumulation (Qu et al., 2015). For similar reasons, manure-derived biochar had higher N content than other feed-stock biochars under identical production conditions (Sun et al., 2011; Yu et al., 2014).

1.3. The role of various characteristics in contamination remediation

In addition to the properties mentioned above, other physical-chemical characteristics of the manufactured biochar include pH, surface charge, electrical conductivity, ash content, particle structure, surface topography and dissolved organic carbon (Rehrh et al., 2016). The effect of biochar on metal behaviors in soil or sediment as related to its characteristics can be classified according to the following three points. Firstly, biochar can bind and adsorb metals through electrostatic adsorption, ion exchange, co-precipitation and the complexing function of oxygen functional groups and π electrons (Sohi et al., 2010; Beesley et al., 2011; Ahmad et al., 2014). Among those adsorption mechanisms, electrostatic adsorption was related to surface charge, ion exchange was controlled by ash content and co-precipitation correlated with alkaline groups and pH value. Due to the abundant pore structure, moreover, the adsorbed metal ions would migrate from outer sphere to inner sphere of the biochar (Houben et al., 2013a; Yin et al., 2016). According to method of partial stripping of components from biochar and comparing the proton concentration before and after adsorption, the contribution of various adsorption mechanisms for Pb have been analyzed; it was shown that approximately 80% of the metal was adsorbed through co-precipitation, 11.4% resulted from oxygen functional groups and only 7.7% was induced by π electrons (Liu, 2014). But in other studies, the surface functional groups were found to contribute more to binding pollutants (Hale et al., 2011; Xu et al., 2016a). Secondly, it is widely known that metal cations are unstable in acidic conditions and stable in alkaline conditions. Therefore, due to the presence of carbonates and
functional groups such as \(-\text{COO}^-\) (\(-\text{COOH}\)) and \(-\text{O}^-\) (\(-\text{OH}\)) contained by the biochars, they can improve metal stability in soil and sediment by increasing the pH value; meanwhile these functional groups are also responsible for the negative charges of the biochars (Yuan et al., 2011). Finally, increasing the DOC content and other dissolved material induced by biochar could stimulate microbial activity and then lead to biochemical processes as well as altering redox conditions, which would have an indirect influence on contaminants (Beesley and Dickinson, 2011; Choppala et al., 2012; Qian et al., 2016).

Generally, all of these properties play different roles in immobilizing metal pollutants, and these parameters are important to the application of biochar for contaminant remediation and for improving ecosystem health. In the following section, the specific influences and functions of these characteristics will be discussed in detail according to the different types of contaminants under given conditions.

### 2. Metal stability and immobility in different matrices amended by biochar

Unlike organic matter, trace or heavy metals cannot be degraded by microorganisms and may exist in environments persistently. As a manufactured absorbent, biochar can immobilize both organic and inorganic materials simultaneously (Cao et al., 2009; Beesley et al., 2010). Generally, biochars with lower specific adsorption are suitable for complex metal ions and complicated organic matter, with sorption occurring on the inner-/outer-sphere sites to reduce pollutant bioavailability and mobility (Houben et al., 2013a; Yin et al., 2016). A number of studies have shown that the capability of biochar to remedy pollution relates not only to the surface physical adsorption and micro-pore structure, but also to the organic components and inorganic ions that may play dominant roles in stabilizing metals (Uchimiya et al., 2011b; Qian et al., 2015; Xu et al., 2016a).

In addition, biochar colloids, defined as active components and dissolved matter, can also affect metal bonding and redox conditions (Qian et al., 2016).

However, previous studies have mainly focused on improving soil and water quality and, until now, sediment remediation by biochar has not yet been extensively utilized or further researched. Therefore, specific investigations and field trials related to metal binding, transformation and release from sediment-biochar systems are urgently needed. In this section, we mainly review the studies on heavy metal adsorption and stabilization by biochar and the bonding mechanisms in aquatic and soil systems. We firmly believe that these applications and studies can be instructive for sediment remediation based on similar mechanisms.

#### 2.1. Metal cations

##### 2.1.1. Cu, Zn, Pb and Cd

Heavy metals such as Cu, Zn, Pb and Cd are common pollutants in water, soil and sediment systems (Beesley et al., 2011; Akcil et al., 2015), and all of these metals are always present as divalent ions or compounds, so their characteristics and behaviors are similar. It would therefore be reasonable to suggest that the metals have similar properties and behaviors in the presence of biochar, even though a few differences do exist (Beesley et al., 2010).

A study in single-contaminant systems demonstrated that four different types of biochar (bamboo-, sugarcane bagasse-, hickory wood- and peanut hull-derived) removed Pb(II) at 18%–35% efficiency, Cd(II) at 11%–18% and Cu(II) at 4%–16%, respectively. The authors suggested that the adsorption of Pb and Cd may be affected by the pore structure, while Cu removal may be related to surface functional groups (Zhou et al., 2013). Tong et al. (2011) found that a rise in pH from 3.5 to 6.0 increased the adsorbed mass of Cu(II), and peanut shell-obtained biochar exhibited a higher capacity for Cu(II) bonding than both soybean straw-/canola straw-obtained biochar and activated carbon. Through Zeta potential and FTIR-PAS spectral analysis, it was found that the biochar surface potentials become more negative and the surface functional groups (e.g. \(-\text{COOH}\) and \(-\text{OH}\)) further dissociated as pH increases, which promotes complex formation and an increasing ability to bind the metals (Tong et al., 2011).

However, in other studies, the sorption mass of Zn(II) always increased with pH, while, unlike Zn(II), the absorption mass of Cu(II) and Pb(II) decreased for pH > 5, which may result from the formation of soluble hydroxyl complexes (Liu and Zhang, 2009; Chen et al., 2011). A linear correlation was observed between cation release and copper immobilization, so if mineral matter can only be sparingly soluble, then precipitation or metal-exchange contributes less to adsorption, which may inhibit pollutant removal (Uchimiya et al., 2011a).

In addition, the ash content of biochar can also affect the sorption behavior of biochar. Generally, the more ash content the biochar has, the higher pH value can be obtained, promoting metal precipitation and immobilization (Mukherjee et al., 2011; Tong et al., 2011; Zhang et al., 2015). Lima et al. (2010) utilized 8 different kinds of biochars for binding Cu(II), Cd(II), Ni(II) and Zn(II), with switchgrass-obtained biochar possessing the greatest ash content and showing excellent capability for pollutant adsorption. However, it is not always the case that higher pH/ash content leads to better sorption behavior for all pollutants. This can be explained by the multiple mechanisms involved in the adsorption process. For example, Mohan et al. (2007) found that the maximum adsorption for As(V) and As(III) occurred at acidic and alkaline condition, respectively, and Pb(II) absorb capability decreased after increasing pH higher than 5 (Liu and Zhang, 2009).

In a multi-contaminant system, a study showed that biochar can dramatically reduce Cd and Zn mobility and concentrations in soil pore water during 60 days of field exposure. In contrast, the concentration of Cu in the pore water was lower until mixing with biochar, at which point the concentration increased more than 30-fold accompanied by a significant increase in dissolved organic carbon (DOC). Subsequently, the Cu(II) concentration gradually decreased as the remediation proceeded. At day 56, its concentration declined to 0.4-fold when compared to the 7-day value (Beesley et al., 2010). The effect of dissolved organic matter on Cu binding was negative, and the increase in dissolved organic carbon with the addition of biochar lead to Cu mobilization, an observation further verified by Park et al. (2011b). In dynamic redox conditions, biochar addition has little effect on redox
processes, and the pH increase is slight. However, concentrations of dissolved metals were considerably lower in biochar-controlled conditions compared with the uncontaminated condition (Rinklebe et al., 2016).

In long-term studies, hardwood-derived biochar was mixed with Cd- and Cu-contaminated soil during 3 years of incubation, and the concentrations of CaCl2-extractable Cd and Cu decreased by 57.9% and 63.8% in the first year, whereas these values further decreased in the following 2 years, which means that biochar aging did not have a negative influence on metal stability, and the biochar performed well to sequester metals (Li et al., 2016). When mixed with soil, the sorption ability of biochar was little affected by pore block, which also suggested that the surface functional groups contribute more to the binding of pollutants (Hale et al., 2011). Moreover, competitive adsorption can be observed in binary polluted systems. When Cu and Zn co-exist in a system, each metal’s behavior can be affected by the other. In an adsorption study, Cu or Zn adsorption was only marginally affected by the presence of another metal at low initial metal concentrations (0.1 mmol/L), whereas at high initial metal concentrations, Zn adsorption capacity decreased by approximately 75%–85% in the presence of Cu >1 mmol/L (Chen et al., 2011). This phenomenon could also be obtained in other binary sorption systems such as Pb and Cd, As and Pb as well as Cd and As (Zhang, 2015). Those results may imply that metals could be adsorbed by the same sites and functional groups, while competing with other metals to produce metals could be adsorbed by the same sites and functional as Cd and As (Zhang, 2015). Those results may imply that binary sorption systems such as Pb and Cd, As and Pb as well as Cd and As (Zhang, 2015).

2.1.2. Hg

Mercury is one of the most hazardous contaminants as characterized by its toxicity, mobility, and long residence time in the environment, and has similar geochemical characteristics in sediment and soil environments including redox reactions, sorption and desorption, methylation and biological processes (Randall and Chattopadhyay, 2013; Xu et al., 2015).

Liu et al. (2016) evaluated 36 kinds of biochars and their ability to remove mercury from aqueous solutions. In this study, biochars produced at higher pyrolysis temperatures exhibited greater removal capability for total Hg (>90%) than those from lower pyrolysis temperature production (<90%). Similarly, Xu et al. (2016a) utilized two types of biochars, bagasse- and hickory chips-based, and activated carbon to adsorb Hg(II), and the results showed that the biochars presented higher sorption capacities than activated carbon. However, in another study (Gomez-Eyles et al., 2013), biochar and activated carbon had equal sorption capability toward methyl mercury, whereas biochar was not better for inorganic Hg than natural sediments. According to spectral and fluorescence analysis, the formation of chemical bonds between Hg(II) and oxygen functional groups dominated the mechanism of Hg(II) removal. Generally, the formation of \((-\text{COO})_2\text{Hg(II)}\) and \((-\text{OH})_2\text{Hg(II)}\) contributed to Hg(II) bonding, and the π electrons of C=O and C=O induced Hg-π binding also play a major role in this process (Xu et al., 2016a). Further X-ray photoelectron spectroscopy analysis indicated that reduction of Hg(II) to Hg(0) by phenol groups or π electrons occurred during the removal of Hg(II) by biochars (Xu et al., 2016). Hg was heterogeneously distributed across the biochar particles and was bound either to S in biochars with high S content or to O and Cl in biochars with low S content (Li et al., 2016).

Furthermore, methylation is an important environmental behavior of mercury; its toxicity and bioaccumulation can be greatly amplified when inorganic Hg is converted to methyl-mercury (MeHg) (Boening, 2000). In a pot experiment (Zhang et al., 2010), mixing MeHg-contaminated soil with 4% biochar reduced the MeHg extraction rate by rice, which could be partly attributed to the strong binding between biochar and MeHg, and increased the MeHg levels in soil. The author also found that biochar amendment results in evident enhancement of the net MeHg production in rice paddy soil. Stimulated microbial activity and thus microbial processes for MeHg production could be mainly responsible for this. In addition, the change of oxido-reduction potential (ORP), total dissolved Fe, sulfate and total number of sulfate-reducing bacteria, which reflect the process of methylation, showed significant correlation with biochar application. Remarkably in this study, despite the increased MeHg concentrations in soil under biochar amendment, significantly lower phytoavailable MeHg levels were observed, leading to lower MeHg accumulation in rice plants. In another study, however, the methylation rate was decreased approximately 80% in biochar-amended sediments as compared to untreated sediment, and the demethylation rates were relatively unchanged (Bussan et al., 2016), which means that biochar curbs the process of methylation. The reasons for these discrepancies have not been revealed, and we speculate that may result from different kinds of biochars having either positive or negative effects on microorganisms and then methylation and demethylation, not only in soil but also in sediment.

2.2. Oxy-anion compounds

Biochars possess a large surface area and are rich in porous regions that can develop dual surface properties, both negative and positive, indicating that biochar can adsorb both negatively and positively charged species, including AsO₄³⁻ and CrO₄²⁻ (Solaiman and Anawar, 2015). In addition, the valence of those oxy-anion species could vary in the presence of biochar, producing adsorption behaviors distinct from the cationic metals discussed above. The major reasons are mainly related to microbial processes, and, as we know, biochar can stimulate microbial activities both in soil and sediment, thus promoting the occurrence of redox reactions.

2.2.1. As

Arsenic(III) and arsenic(V) are the common forms of arsenic, and arsenite and arsenate are the major forms of arsenic in water, soil and sediment systems (Fischwasser, 1990). Among metalloids, arsenic is most likely to mobilize in alkaline conditions in both oxidizing and reducing systems, and redox potential and pH control arsenic speciation (Mohan et al., 2007).

After biochar application to soil, As concentrations in pore water increase, which is closely related to the increase in pH induced by biochar. Moreover, both Cu and As have been
observed to be strongly positively correlated with the DOC introduced by biochar application, indicating co-mobilization (Beesley and Dickinson, 2011). Beesley et al. (2010) also suggested that multi-contaminated soil remediated with biochar increased the As and Cu concentration in pore water, which was the opposite of the results for Cd and Zn. The result showed that DOC was the main reason for Cu increase, whereas pH was responsible for As mobilization (Beesley et al., 2010). This was further supported by Yin et al. (2016) who found that the As concentration in a KH₂PO₄ extract was increased by 6.43%–16.7%, and this enhancement was proportional to the biochar effect on increasing soil pH. Increasing mobility of As results from the competition of OH⁻ with HASO₄²⁻ for binding sites under alkaline conditions, so that subsequent release of As is promoted due to the relatively lower anion exchange capacity (Inyang et al., 2010; Yin et al., 2016). Further, during 49 days of incubation in an anoxic sediment-water microcosm, Chen et al. (2016) found that the detectable As(III) levels approached the As(total) levels, and suggested that abiotic effects were responsible for 10% – 13% and biotic effects for 87% – 90% of these observed values. The main reason for this was the enhancement of DOC bioavailability by biochar, which stimulated bacterial activity (specifically for the species Geobacter, Anaeromyxobacter, Desulfosporosinus and Pedobacter), thereby enhancing As mobility (Ahmad et al., 2014; Chen et al., 2016). Even so, in aqueous solution biochar has demonstrated a strong ability to remove As effectively (Mohan and Pittman, 2007).

### 2.2.2. Cr

Like arsenic, Cr also presents a dual valence in sediment and soil systems, trivalent and hexavalent; Cr(VI) is highly toxic and carcinogenic even at very low concentrations, whereas Cr(III) is nontoxic and always strongly bound to matrix particles. Unlike the adsorption behaviors of the cationic metals toward biochar, the removal capacity of Cr(VI) was decreased significantly with increasing solution pH, and the highest removal capacity of Cr(VI) was obtained under low pH conditions (Dong et al., 2011). Thus, Cr(VI) is more mobile in alkaline conditions than in acidic conditions. However, the alteration of redox potential by biochar leads to Cr(VI) being reduced to Cr(III) in the presence of oxygen-containing organic components or other electron-donor groups (Park et al., 2007). Unlike arsenate, the reduction rate of Cr(VI) is relatively lower in alkaline soil, and application of biochar can decrease the availability and mobility of Cr in soil pore water (Choppala et al., 2012, 2016). Through FT-IR analysis, the C-O-C₆H₅ (methoxyl) deformation and C-OH (hydroxyl) in phenolic structures were shown to be responsible for Cr(VI) reduction, while mineral matter and other oxygen functional groups such as carbonyl promoted the Cr(VI) reduction and adsorption by biochar (Hsu et al., 2009; Choppala et al., 2012). Generally, biochar could promote the reduction of As(V) to As(III), thereby increasing its bioavailability, toxicity and mobilization. On the contrary, the reduction of Cr(VI) to Cr(III) induced by biochar reduced the bioavailability and toxicity of Cr (Choppala et al., 2016). Thus, the effects of biochar on the redox of Cr and As are similar, but the result can be said to be significantly different.

### 3. Potential effects of biochar on biological systems during remediation processing

Using biochar as an amendment for in-/ex-situ remediation of soil and sediment should take into account not only the pollutant’s binding performance, but also the system’s ecological aspects such as long-term stability and ecological impact, which in turn are reliant on the properties and specific characteristics of biochar types (Beesley et al., 2011; Akcil et al., 2015). However, the literature indicates that soil remediation by biochar has been mainly concerned with issues related to revegetation, soil fauna and microorganisms, whereas previous studies have only focused on microorganisms in aqueous and sediment systems (Gomez-Eyles et al., 2013; Chen et al., 2016; Liu et al., 2017).

#### 3.1. The effect of biochar on plant growth

It is well known that biochar is a good soil modifier to promote plant growth and enhance crop yield, but those beneficial consequences have only been studied and obtained over the course of a few years, therefore the long-term effect has not been confirmed (Griffin et al., 2017; Laird et al., 2017). Thomas and Gale (2015) studied growth responses of trees to biochar addition through meta-analysis of reviews and other studies. Their work indicated that positive responses are obvious, especially at early stages of growth, and appear to be more common in boreal and tropical settings than in temperate environments. The mean increase in biomass from this analysis was up to 41%. More specifically, in a tomato pot experiment (Herath et al., 2015), the common diagnostic symptoms of heavy metal phytotoxicity, such as leaf chlorosis, necrosis, leaf epinasty and growth retardation, were observed in plants cultivated in unamended soil but not in amended soil. The biomass of tomatoes grown in biochar-amended soil at a 5% application rate was increased by approximately 40-fold over those in the unamended soil. Both the biochar fertilizing effect and immobilization of heavy metals in the soil contributed to this phenomenon (Houben et al., 2013b; Herath et al., 2015). The influence of biochar on plant growth was further studied by Rees et al. (2016), who observed that biochar application increased shoot and root biomass and root surface, and a decreased ratio of shoot-to-root mass indicated that root proliferation improvements resulted from biochar application.

Similar results have been obtained from other congeneric studies (Graber et al., 2010; Brennan et al., 2014; Prendergast Miller et al., 2014; Rees et al., 2016), and the related mechanisms and effects associated with biochar utilization can be summarized as follows: (1) elevation of water holding and availability, (2) provision and amelioration of organic matter and nutrient retention and bioavailability necessary for plant growth, (3) amelioration of soil permeability conducive to root proliferation, and (4) lowering of the phytotoxicity of metal pollutants. In addition to those beneficial influences, negative results can also occur with biochar application, such as inhibition of plant growth. The reasons for this may relate to biochar’s decrease of the availability of nutrients in unfertilized soils due to stronger adsorption (Beesley et al., 2011), and the high concentrations of metals in the soil could...
bind to organic matter and inhibit its biodegradation so as to reduce its bioavailability (Bolan et al., 2014). However, those disadvantages could be offset by selecting N-rich feedstock like poultry manure (Yu et al., 2014) and combining biochar utilization with compost or fertilizer amendments (Beesley et al., 2010).

3.2. The effect of biochar on fauna habits

Unlike plants, the information on fauna in soil or sediment amended by biochar is quite limited. In other reviews (Lehmann et al., 2011; Solaiman and Anawar, 2015), the authors concluded that earthworms contributed to grinding biochar and mixing it into soil, while the population also adapted to the consumption of charred material, which affected them in favorable ways. However, Li et al. (2011) observed in their study that earthworms avoided soils containing 100 and 200 g/kg dry biochar at statistically significant levels. The reasons for this do not appear to be associated with nutritional deficiency or the presence of pollutants, but were based on insufficient moisture. Similarly, increasing pH caused by biochar has been shown to have negative influences on the earthworm population (Weyers and Spokas, 2011). In addition, Bastos et al. (2014) assayed the potential risks to aquatic ecosystems exposed to runoff and leachates from biochar-amended soils. The result indicated that Daphnia magna upon exposure to 50% and 100% soil-biochar extract concentrations had 20% and 25% mobility impairment.

3.3. The effect of biochar on microorganism community

The changes in sediment and soil properties induced by biochar can alter overall system conditions, including abiotic factors (e.g. available carbon, nutrients, pH, toxic matter and water content) and biotic factors (e.g. different habitats may lead to changes in community composition and structure) (Lehmann et al., 2011). Compared to plants and fauna, studies focusing on the effect of biochar addition on microorganisms are relatively abundant and extensive, and most indicated that microbial biomass and microbial activity in biochar amended soil and sediment had been promoted (Steinbeiss et al., 2009; Zhang et al., 2010; Choppala et al., 2012; Ahmad et al., 2014; Chen et al., 2016; Liu et al., 2017). In general, the porous structure of biochar can provide habitat for microbial communities, which protects them from grazers, and the soluble organic carbon and other nutrients adsorbed by biochar can supply required substrates (Atkinson et al., 2010; Beesley et al., 2011). Recently, Jain et al. (2016) investigated the effect of overburden collected from a mine area remediated with biochar on the resistance and resilience of soil enzymes responsible for nutrient cycling. The results indicated that biochar addition enhanced the enzymes’ resistance and resilience in the contaminated soil. In addition, Cui et al. (2016) found that mushroom-derived biochar addition resulted in a higher removal rate of antibiotic resistance genes and pathogenic bacteria during manure composting when compared to rice straw-derived biochar. Hence, addition of different biochars led to different microorganism community distributions associated with the adsorbed nutrients on biochar surfaces, by increasing or suppressing the specific microbial community (Muhammad et al., 2014; Cui et al., 2016). Thus, the stronger binding capability of biochar for nutrients and organic matter may result in a negative influence on microbial activity as well as plants (Beesley et al., 2011).

With respect to aquatic microbial communities, the results are theoretically similar. Smith et al. (2012) investigated the potential harmful effect of biochar water-extractable substances on the growth of blue-green algae and eukaryotes. Water extracted from pine wood-derived biochar showed a great inhibitory effect on aquatic photosynthetic microorganism growth, for which the active components of the compounds could pass a membrane with 500-delta cutoff pore size, while chicken litter and peanut shell-derived biochar water extracts showed no signs of growth inhibition. Bastos et al. (2014) further suggested that exposure to soil-biochar leachates can result in species-specific effects and dose-response patterns, and also observed that the marine bacterium Vibrio fischeri responded to aqueous extracts with sensitivity, while the extract fractions had no effects on the growth of the microalgae Pseudokirchneriella subcapitata.

3.4. The potential risk of biochar application on biological systems

Therefore, it seems that biochars could induce both positive and negative effects on plants, fauna and microorganisms. These phenomena may be decided by the characteristics of biochar and ambient conditions. Although the potential benefits of biochar have been confirmed by several studies as previously discussed, the potential risk and hazards have not been fully understood. This issue has not been discussed in detail except by Kuppusamy et al. (2016) and Ogbonnaya and Semple (2013).

One of the unintended consequences induced by biochars was the direct toxic effect on organisms through its self-contained organic or inorganic pollutants, whose negative aspects were mainly man-made and well controllable and should be further investigated. A study has already demonstrated that heavy metal-rich biochar could significantly increase NH₄NO₃-extractable Cd in contaminated soils (Shen et al., 2016), and another has shown that both feedstock and production parameters affected the content of heavy metals in biochar (Qu et al., 2015). Moreover, PAHs may be compounded during the manufacturing process, in which feedstock and heat treatment temperatures are the key aspects related to these substances. The pyrolysis temperatures also were recommended to be more than 600 °C for low toxicity, and not all biochars made from different feedstocks are suitable for agricultural applications. These biochars may have poor capability for retaining nutrients and are susceptible to microbial decay (Ogbonnaya and Semple, 2013; Qiu et al., 2015; Kuppusamy et al., 2016).

On the other hand, it is the excellent properties of biochars, including enhancement of nutrient use efficiency and water holding ability and improvement of soil texture, that attract our attention. However, the excellent sorption capability of biochar may deactivate agrochemicals like pesticides and herbicides and compete for nutrients with plants, reducing their bioavailability (Yao et al., 2012a; Kuppusamy et al., 2016). Besides, binding of contaminants by biochar limits their...
availability for microbial degradation and remediation, which may cause the greatest environmental impact in the long-term (Beesley et al., 2011).

Moreover, due to changes in nutrient bioavailability, environmental factors and habitat, some microbial groups either become competitively dominant or are constrained, leading to changes in community composition and structure, and biochar has not always been beneficial to soil microbial abundance (Lehmann et al., 2011; Kuppusamy et al., 2016). Changes involving increase and decrease in the community composition and structure of microorganisms have already been witnessed by several studies (Jindo et al., 2012; Chen et al., 2013; Xu et al., 2016b). Mechanisms related to these influences are still unclear and may lead to possible disadvantages in using biochar for soil and sediment management, in which the beneficial community could not compete with other organisms, even harmful ones.

Since remediation engineering aims to attain an all-around positive result as far as possible, the appendant negative effects of biochar should be intentionally avoided, mainly through controlling feedstock and optimizing the manufacturing process, and other materials can also be applied together with biochar, for instance, sand, calcite, zeolite, organoclay, biopolymers and so on (Zhang et al., 2016), to increase the types of contaminants to be treated and strengthen the stability and compatibility with surroundings.

4. Using biochar for sediment management: a potential strategy

As mentioned in the first section, sediment management relates to two approaches, in-situ and ex-situ processes. For ex-situ processes with biochar, the remediation involves dredging, pretreatment, stabilization and final disposal, as shown in Fig. 1. These processes are closely associated with metal-contaminated soil remediation, which also includes stabilization of contaminants and reducing their bioavailability (Yao et al., 2012b), and studies concerning soil remediation by biochars as well as their effects on biological systems have already been discussed in prior sections. We firmly believe that these applications and studies can be helpful and instructive to sediment remediation due to the similar mechanisms for metal binding and stabilization. Therefore, here we mainly consider in-situ processes using biochars.

Capping is the most commonly used alternative for the in-situ remediation of sediments. Using biochar (as well as activated carbon) as an active cap material is a new technology and direction in contaminated sediment management (Ghosh et al., 2011), which can effectively decrease contaminant flux from sediment to the overlying water and thus isolate contaminants from the bioactive portion of the cap for decades to centuries (Murphy et al., 2006; Josefsson et al., 2012; Zhang et al., 2016). Active capping means using chemically reactive materials to sequestrate contaminants, reduce their mobility, toxicity and bioavailability, offering both containment and treatment to the contaminated sediment (Zhang et al., 2016), and thus reduce pollutant accumulation in the aquatic food-chain. In addition, effective capping materials also should be provided with the characteristics of erosion resistance and lower or beneficial impacts on benthic organisms. To the best of our knowledge, there have been no studies applying biochar as an active cap to remediate contaminated sediments, let alone combined with other materials. Thereby, here we provide a modified conceptual model (Fig. 3) of how biochar can be used as an active sorbent
to reduce metal contaminant bioavailability and flux from sediment to overlying water (Ghosh et al., 2011).

As shown in Fig. 3, metals in contaminated sites may mobilize into overlying water, and be accumulated and amplified in organisms through the food chain without any protection, involving plant root uptake, benthonic fauna surface adsorption and digestion and aquatic animal predation. If contaminated sediments were covered with biochar, as an active amendment, the thin capping strategy would impede or even cut off the path for metal release from sediment into the water column. Bio-distribution and other natural mixing processes promoting homogenization between sediment and biochar can further improve the immobilization of metal contaminants (Sun and Ghosh, 2007). Over the long term, the biochar layer could be covered with clean new sediment deposit to serve as another barrier to curb the release of metals.

However, study has shown that an active capping layer may be transported downstream without any protection, and if it were covered with a gravity-stable layer, the erosion rate could be dramatically reduced (Zhang et al., 2016). For example, the density of sand and gravel are greater than biochar, so those gravity-stable matters can protect the biochar capping layer structure from erosion and becoming thinner (Fig. 3), and materials such as calcite, zeolite, apatite, organoclay and biopolymer can also be used to achieve multiple goals (Knox et al., 2012; Zhang et al., 2016). Besides, the gravity-stable layer also provides a habitat for benthic organisms to colonize (Lampert et al., 2013).

Furthermore, the settling property of biochar is an important consideration when using biochar to cap contaminated sediments. The low density of biochar makes it difficult to deposit spontaneously to bottom areas, especially in faster flowing sites. Thus, a reactive core mat for improving the settling property of low-density materials could inhibit the floating of an active layer encapsulated in two fixed layers (McDonough et al., 2007; Dogus et al., 2011). As depicted in Fig. 3, the reactive core mat containing biochar or a mixture of materials is confined between two permeable geotextile layers. Commonly, the geotextiles are manufactured with biodegradation-resistant synthetic fibers into flexible and porous fabrics. Consequently, the geotextile prevents mixing of biochar with sediments to reduce its immobilization and biological effects. If the bed layer of geotextile could be designed using dissolvable substances or biodegradable matters, the comprehensive effect of remediation may be more desirable.

### 5. Recommendations for future research

Biochars have been recommended as carbon-neutral or even carbon-negative materials and have demonstrated excellent potential for reduction or immobilization of metals in contaminated soil and sediment. However, as a potential technology, many aspects still need to be developed and examined for both ex- and in-situ application, especially for sediment remediation. Several variable aspects are involved in determining the characteristics and properties of biochar in terms of physical and chemical attributes and the related effects on matrix systems. Specifically, further research is needed in the following areas:

1. Standardization of the production process depends on the application purpose and the types of feedstock, and will include selection of feedstock and determination of optimal pyrolysis temperature. In addition, it may be necessary to modify the manufacturing methods and conduct feedstock pre-treatment to develop clean biochar materials free of any harmful substances.

2. In terms of ex-situ remediation, much study is needed in a number of research areas, including (a) comparison of the physicochemical properties of the soil(sediment)-biochar compound (SBC) before and after mixing, (b) study of the binding capability and adsorption mechanisms of the SBC for heavy metals or metalloids, (c) measurement of the metal speciation features and bioavailability in the presence of biochar at different time scales, (d) testing of the toxic effects of exposing soil and aqueous biota to SBC or its water extractives, (e) investigation of the potential risks of SBC under extreme conditions, such as (acidic) rain/water leaching and soaking, super drying and intense disturbance, (f) examination of the possibility that SBC works as a soil additive and, subsequently, the responses of plant, fauna and microorganism communities, and (g) exploring the ultimate application and disposal of SBC (for example, dumping into soil or rivers), or the requirements for further modification as a raw material to other industries.

3. With respect to in-situ amendments, the execution scheme and stability of the sediment-biochar-pollutant system should be deliberately planned and cautiously explored. Specifically, in the sediment matrix (a) various pilot-scale tests are needed to determine how to conduct remediation and where the technology is best suited or unsuited and where there is need for support by other methods, (b) the quality of the overlying and pore water and the mass transfer of metals should be measured or calculated among the sediment, biochar and water, (c) the related fundamental mechanisms of metal binding and immobilization with SBC should be better understood, (d) ecosystem scale effects, recovery and assessment should be studied, and (e) the effects of biochar application on nutrient and carbon cycles, habitat, food-web and geochemical processes also need to be interpreted.

4. Long-time stability needs more research, as a continuing topic of interest in restoration science. In field studies, the durability and metal-binding capability must be further demonstrated. In addition, questions to be answered include how the aging process and pore blocking by biotic or abiotic matter occurs and how subsequent chain-effects could be predicted and prevented.

### 6. Summary

It is widely accepted that biochar can effectively reduce the mobility and bioavailability of metals. Meanwhile, modern environmental management and remediation strategies are
paying more attention to long-time stability and to the effects of the most toxicologically relevant fractions of contaminants and the ecological responses, and biochars have demonstrated their superiority as suitable candidates for a successful and sustainable remediation strategy.

However, most studies of biochar application have focused on soil management, in which biochar has already shown its capability to bind metals, decrease contaminant mobility and bioavailability, stimulate microorganism activity and promote soil revegetation and recovery. In parallel to these studies, relevant research on sediment remediation by biochar is limited and just at the beginning stages, especially as these sediment restoration projects also relate to sustainability, efficiency and eco-compatibility. Other char materials, such as activated char that is similar to biochar, have already been successfully used as sorbent amendments in contaminated sediments both in trial-scale and pilot-scale to study their feasibility, persistence, binding potential with pollutants and reduction of sediment porewater contaminant concentrations as well as sediment-to-water fluxes. These studies have therefore provided an instructive way forward for biochar application in sediment management. Considering biochar use as a “multi-win” amendment, it is reasonable and reliable to utilize it as an amendment to implement soil remediation and sediment management. Finally, we have ample reason to believe that biochar is a low-cost and environmentally friendly amendment for heavy-metal contaminated site remediation.

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