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Indispensable role of biochar-inherent mineral constituents in its environmental applications: A review

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Abstract

Biochar typically consists of both carbon and mineral fractions, and the carbon fraction has been generally considered to determine its properties and applications. Recently, an increasing body of research has demonstrated that mineral components inherent in biochar, such as alkali or alkaline earth metals in the form of carbonates, phosphates, or oxides, could also influence the properties and thus the applications. The review articles published thus far have mainly focused on multiple environmental and agronomic applications of biochar, including carbon sequestration, soil improvement, environmental remediation, etc. This review aims to highlight the indispensable role of the mineral fraction of biochar in these different applications, especially in environmental applications. Specifically, it provides a critical review of current research findings related to the mineral composition of biochar and the effect of the mineral fraction on the physicochemical properties, contaminant sorption, carbon retention and stability, and nutrient bioavailability of biochar. Furthermore, the role of minerals in the emerging applications of biochar, as a precursor for fuel cells, supercapacitors, and photoactive components, is also summarized. Overall, inherent minerals should be fully considered while determining the most appropriate application for any given biochar. A thorough understanding of the role of biochar-bound minerals in different applications will also allow the design or selection of the most suitable biochar for specific applications based on the consideration of feedstock composition, production parameters, and post-treatment.

1. Introduction

Biochar, a carbon-rich byproduct of biomass pyrolysis, is receiving increasing attention due to its multiple functions in carbon sequestration, reduction of greenhouse gas emissions, soil improvement, environmental remediation, etc. (Beesley et al., 2011; Lehmann et al., 2011). It has been commonly assumed that the carbon fraction of biochar plays a dominant role in its applications (Chen et al., 2008a; Lee et al., 2010). For example, the stable and rich aromatic forms of the C fraction enable biochar to be used as a means of sequestering atmospheric CO_2 (Lehmann, 2007); because of its high organic C content and porous structure, biochar has the potential to serve as a soil conditioner to improve the physicochemical and biological properties of soils (Ippolito et al., 2012a); partitioning and adsorption by the carbon fraction of biochar could be effective sorption mechanisms for organic contaminants (Chen et al., 2008a); complexation with organic O-containing functional groups, such as -COOH, alcoholic-OH, or phenolic-OH groups, is involved in heavy-metal sorption by biochars (Lu et al., 2012).

In addition to the rich carbon fraction, biochar often contains high levels of mineral (ash) components, such as alkali metals (K, Na, etc.) or alkaline earth metals (Ca, Mg, etc.), which are often present in the form of carbonates, phosphates, or oxides (Cao & Harris, 2010; Xu et al., 2014). Compared to the carbon fraction, the role of the mineral fraction in biochar applications has received less attention, probably because (1) the biomasses used for the generation of biochar are mostly plant residues, which contain limited mineral components (e.g., woody biomass) (Hale et al., 2016); and (2) demineralization or de-ashing treatments are often applied to remove the mineral fraction from the original biochar before it is used (Tan et al., 2015). However, with the

49   testing of more feedstock for biochar applications, it has become apparent that mineral

50   fractions could influence the properties of biochar and thus directly or indirectly

51   influence its applications (Buss et al., 2016b; Gunes et al., 2015; Yuan et al., 2011). For

52   example, mineral components, such as Ca, Mg, K, and P, may allow biochar to act as a

53   direct source of mineral nutrients, promoting plant growth (Amini et al., 2015); anions

54   such as OH^-, CO_3^{2-}, PO_4^{3-} and SO_4^{2-}, released from biochar minerals, play an important

55   role in the removal of heavy metals by the formation of metal precipitates (Inyang et al.,

56   2015). On the other hand, high contents of certain minerals, especially toxic heavy

57   metals, in the biochar could raise health concerns (Buss et al., 2016a) and could also

58   limit the sorption of organic compounds if these biochars are not de-ashed prior to their

59   use in applications requiring the sorption of organic compounds (Sun et al., 2013;

60   Zhang et al., 2013a).

61   A variety of aspects of biochar, including its production, properties, and

62   applications, have been reviewed extensively (Xie et al., 2015; Inyang et al., 2015).

63   However, there is no review dealing with the role of the mineral fraction of biochar in

64   its properties and applications. This paper aims to present a critical review of the

65   indispensable role of biochar inherent mineral fractions in controlling its properties and

66   applications, especially environmental applications. Specifically, the effect of the

67   mineral fraction on the following aspects will be systematically reviewed: (1)

68   physicochemical properties of biochar, (2) contaminant sorption by biochar, (3) carbon

69   retention and stability of biochar, (4) nutrient bioavailability of biochar, and (5)

70   emerging applications of biochar as a precursor for fuel cells, supercapacitors, and

71   photoactive components.

72   **2. Mineral constituents in biochar as a function of feedstock and pyrolysis**

conditions

74　　　Almost any form of organic material, such as crop residues, forestry byproducts,

75　urban yard wastes, industrial byproducts, animal manure, and sewage sludge, can be

76　converted to biochar by pyrolysis under a wide range of conditions (Kuppusamy et al.,

77　2016). The key parameters of the pyrolysis process include the peak temperature,

78　holding time at peak temperature, heating rate, etc. The variability in feedstock and

79　pyrolysis conditions has a significant effect on the content and form of minerals in

80　biochar (Zhao et al., 2013; Zhao et al., 2015). The mineral (ash) content of biochars

81　derived from different feedstock is shown in Table S1. In general, the mineral content of

82　sludge biochar is normally above 30%, and can reach up to 90%. For manure biochar,

83　the mineral content ranges from 20% to 80%. Biochars derived from plant residues

84　contain much less minerals than sludge and manure biochars (Zhao et al., 2013), with

85　content mostly below 20%. Table 1 summarizes the most common mineral elements,

86　including K, Ca, Mg, N, and P, present in 63 different biochars. K, Ca, Mg, N, and P are

87　all present in high concentrations in manure biochar, and the content of Ca and Mg is

88　higher than that in plant-residue biochar and sludge biochar. Sludge biochar contains

89　more N and P than crop-residue biochar, while the latter contains a higher content of K.

90　Prakongkep et al. (2013) showed that K-minerals in biochars derived from rice husk

91　included archerite (KH_2PO_4), chlorocalcite ($KCaCl_3$), kalicinite ($KHCO_3$), pyrocoproite

92　($K_2MgP_2O_7$), struvite-K ($KMgPO_4·6 H_2O$), and sylvite (KCl). The most common

93　minerals present in biochars include sylvite (KCl), quartz (SiO_2), amorphous silica,

94　calcite ($CaCO_3$), hydroxyapatite ($Ca_5(PO_4)_3OH$), and other mineral phases such as Ca

95　phosphates, anhydrite, various nitrates, and oxides and hydroxides of Ca, Mg, Al, Ti,

96　Mn, Zn, or Fe (Lehmann & Joseph, 2009). These mineral compounds exist either as

97 discrete mineral phases or are associated with the surface functional groups of biochars

98 (Wang et al., 2015).

99   The mineral content of biochar generally increases with increasing pyrolysis

100 temperature (Table 1). For example, Song et al (2012) reported that the content of K,

101 Ca, Mg, and P in biochars derived from poultry manure increased by 32.0%, 30.9%,

102 30.1%, and 34.4%, respectively, when pyrolysis temperature increased from 300 °C to

103 600 °C. This is because as the pyrolysis temperature is increased, the organic

104 constituents of biomass, including cellulose, hemicelluloses, and lignin are, to a large

105 extent, converted and released in the form of volatiles and gases while the much less

106 volatile mineral compounds, such as Mg, Ca and P, remain and are thus concentrated in

107 biochar (Zhang & Wang, 2016). In addition to the enrichment caused by the increase of

108 pyrolysis temperature, the minerals in biochars may also become more crystallized and

109 less soluble, especially above 500 °C (Cao & Harris, 2010; Yuan et al., 2011).

110 Therefore, the solubility of mineral components reduces with increasing temperature, as

111 shown in Table 1. Wang et al. (2015) reported that the soluble PO_4^{3-}-P in peanut-shell-

112 derived biochar decreased from 430 to 70 mg kg^{-1} when the pyrolytic temperature

113 increased from 300 °C to 600 °C, due to the formation of less soluble crystalline

114 phosphates, such as $Ca_2P_2O_7$ and Mg_2PO_4OH, in high-temperature biochars.

115 Additionally, new mineral species may also be formed as the pyrolysis temperature is

116 increased. Qian et al. (2016) showed that new minerals, such as magnesia calcite

117 ($MgCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), appeared in rice-straw biochar

118 when the production temperature was increased from 100 °C to 500 °C.

119   In addition to the above-mentioned "good" mineral elements, biochar may contain

120 some "bad" mineral elements, i.e., potentially toxic elements. The content and

121 availability of these elements is also significantly affected by the feedstock and

122 pyrolysis conditions of biochar. Buss et al. (2016a) and Khanmohammadi et al. (2015)

123 found that the percentage of available, potentially toxic elements, such as Cr, Ni, Cu

124 and Zn, increased with increasing pyrolysis temperature, particularly when the

125 temperature was increased from 600 °C to 750 °C.

126   Both feedstock and production conditions are important for determining the

127 mineral constituents of biochar, but the content of key minerals in biochar shows a

128 linear dependence on the levels within the initial feedstock (Alexis et al., 2007). This

129 suggests that the selection of biochar for soil amendment, aimed at improving soil

130 fertility by the addition of nutrients, should preferentially focus on feedstock selection

131 rather than the production temperature, although the pyrolysis temperature can affect the

132 availability of nutrients in biochar (Zhao et al., 2013).

133 **3. Effect of minerals on the physical and chemical properties of biochar**

134   Mineral elements, such as K, Na, Si, Mg, and Ca, can be involved in the

135 carbonization processes of biomass, thus influencing the pyrolysis reactions and

136 products (Chen et al., 2008b; Yang et al., 2006).Chen et al. (2008b) studied the catalytic

137 effects of inorganic additives on the pyrolysis of pine wood sawdust, pointing out that

138 Na additives could greatly increase the yield of solid products (biochar) and decreased

139 yield of gaseous products. Yang et al. (2006) showed that K_2CO_3 inhibited the pyrolysis

140 of hemicellulose while enhanced the pyrolysis of cellulose by shifting the pyrolysis to a

141 lower temperature. This obvious catalytic effect of K_2CO_3 might be attributed to certain

142 fundamental changes in terms of chemical structure of hemicellulose or decomposition

143 steps of cellulose in the course of pyrolysis. As a result, mineral-induced pyrolysis

144 reactions of biomass may affect the physical and chemical properties, such as the pH,

145 electric conductivity (EC), cation exchange capacity (CEC), specific surface area

146   (SSA), structure, and morphology, of biochar (Zhang & Wang, 2016). This section

147   focuses on the relationship between the biochar mineral (ash) and its key properties.

148   The International Biochar Initiative (IBI) has graded biochar into three classes,

149   based on the carbon content: Class 1 biochar contains 60% carbon or more; Class 2

150   biochar contains 30%-60% carbon; and Class 3 biochar contains 10%-30% carbon

151   (http://www.biochar-international.org/sites/default/files/Guidelines_for_Biochar

152   _That_Is_Used _in_Soil_Final .pdf.). This IBI classification is based on organic C

153   rather than the total C. Since the content of organic C in biochar is much larger than

154   inorganic C, total C is used to represent organic C for the classification in this study.

155   Figure 1a and Table S1 summarize the negative relationship between the carbon content

156   and mineral content (R^2=0.76), showing that most Class 1 biochars contain less than

157   20% minerals; Class 2 biochars contain 20%-60% minerals; and the mineral content of

158   Class 3 biochars is higher than 60%. Therefore, in order to discuss the effect of minerals

159   on the properties of biochar, we also categorize biochar into three classes, based on the

160   mineral content. These include: Class 1 biochar (below 20% minerals), Class 2 biochar

161   (between 20% and 60% minerals), and Class 3 biochar (containing 60% minerals or

162   more). Note that this classification may not map exactly with the IBI classification, e.g.,

163   some biochars may have low ash content as well as a low carbon content due to high H,

164   N, and O contents. However, the carbon content of most biochars is negatively related

165   to the mineral content (R^2=0.76), based on the 278 biochar samples summarized in this

166   papers (Table S1). Therefore, this classification is acceptable for the present review.

167   *3.1. C content*

168   For Class 1 biochars, mostly derived from plant residues, no strong correlation

169   between mineral content and carbon content is observed (Table 1, Table S1, and Fig.

170 1a). This is likely due to the low mineral content, because of which its effects can be

171 masked by those of other constituents, e.g., H, O, and N. However, as the mineral

172 content increases (Class 2 and Class 3 biochars), a strong negative correlation between

173 carbon content and ash content can be observed (Fig. 1a). Singh et al. (2010) found that

174 the C values in low-ash biochar increased with the increase in pyrolysis temperature,

175 whereas the reverse trend was found for high-ash biochar. This discrepancy was due to

176 the dramatically different contents of ash, which was not volatilized and enriched with

177 increasing temperature (Zhang & Wang, 2016). Minerals not only influence the carbon

178 content of biochar but also affect the distribution of carbon in the surface and bulk. Sun

179 et al. (2013) found that after de-ashing the surface C content of manure-derived biochars

180 decreased while the total C increased. However, the authors also noted that this was not

181 the case for biochar derived from plant residues, in which inherent minerals had no

182 discernible effect on the spatial distribution of carbon (Sun et al., 2013). Therefore, the

183 nature and distribution of minerals in biomass play important roles in the content and

184 distribution of carbon in the resulting biochar.

185 *3.2. pH*

186 For biochars of all three classes, most of them were alkaline (pH>7.0) (Fig. 1b).

187 Yuan et al. (2011) and Hass et al. (2012) showed that alkali metals (Na, K) or alkaline

188 earth metals (Ca, Mg) in the form of carbonates are the main alkaline substances

189 responsible for the high pH of biochar derived from crop residues and chicken manure.

190 In their work, a positive correlation between the alkalinity of biochar and its ash content

191 was observed. However, Fig. 1b shows a weak correlation between ash content and pH.

192 Xu et al. (2016b) found that sludge biochar had a much higher mineral content than

193 wheat-straw biochar, but its pH was lower. This can be explained by the abundance of

194   Fe in sludge biochar, since Fe may cause hydrolysis, producing H^+ in the solution.

195   Therefore, the mineral composition, rather than content, has a greater effect on the pH

196   of biochar. Functional groups such as $-COO^-$ ($-COOH$) and $-O^-$ ($-OH$) also contributed

197   to the alkalinity of the biochars, especially for those generated at the lower temperature

198   (Yuan et al., 2011). The pH of biochar samples increased with increasing pyrolysis

199   temperature. This is because a higher pyrolysis temperature can remove acidic

200   functional groups (e.g. $-COOH$ and $-OH$) and promote the separation of minerals such

201   as KOH, NaOH, $MgCO_3$, and $CaCO_3$ from the solid carbon matrix, resulting in elevated

202   pH values (Meng et al., 2013; Mohan et al., 2014). Furthermore, the existence of these

203   alkaline minerals enhanced the buffering capacity of biochar (Xu & Chen, 2014).

204   *3.3. Porosity*

205   Class 1 biochars with a low mineral content show a higher specific surface area

206   (SA, up to 650 m^2 g^{-1}) and pore volume (PV, up to 1.40 cm^3 g^{-1}) than Class 2 and 3

207   biochars (SA, below 200 m^2 g^{-1}; PV, below 0.45 cm^3 g^{-1}), indicating that a high ash

208   content could reduce the surface area and pore volume of biochar (Fig. 1c). It was

209   reported that ash in biochar might fill or block access to micropores (Agrafioti et al.,

210   2013). Sun et al. (2011) found that animal-waste biochars had a lower surface area than

211   plant-based biochars produced at the same pyrolysis temperature and residence time due

212   to the higher mineral contents of most animal-waste biochars. The surface area and pore

213   volume of carbonaceous materials can be greatly improved by base- or acid-treatments

214   since the base-leaching procedure can effectively remove ash (mostly silica) and the

215   acid-washing procedure can act as a cleaning process to remove metallic impurities

216   (Liou & Wu, 2009). Therefore, high-surface-area biochar can be produced from high-

217   ash biochar by de-ashing of the char.

3.4. Surface chemistry

219   Minerals can also influence the surface electrochemistry and ion-exchange

220   properties of biochar. Buss et al. (2016b) found that the electric conductivity (EC) of

221   biochars (used for approximation of salinity) was well-correlated with the ash content

222   ($R^2 = 0.75$). Zhao et al. (2015) found that the point of zero charge (PZC) of plant-based

223   biochars was lower than that of solid-waste-based ones, probably due to the low content

224   of minerals. Minerals such as SiO_2 were highly negatively charged, even at lower pH

225   values due to their low isoelectric point ($\sim$2.0) (Waseem et al., 2010). The cation

226   exchange capacity (CEC) and anion exchange capacity (AEC) also showed strong

227   positive correlation with soluble cations and anions, respectively (Zhao et al., 2015).

228   As discussed above, minerals can affect the physicochemical properties of biochar.

229   Thus, engineered biochar was designed by impregnation of minerals (Yao et al., 2013;

230   Zhang et al., 2012) or by using a demineralization treatment to impart or improve the

231   desirable properties of biochar (Liu et al., 2015).

232   **4. Role of minerals in the sorption of contaminants**

233   The removal of organic and inorganic contaminants from water and soil has been

234   extensively reviewed (Inyang et al., 2015; Mohan et al., 2014; Tan et al., 2015). This

235   section focuses on the role of the mineral components of biochar in the sorption of

236   contaminants, including heavy metals, organic contaminants, N and P, acidic gases, etc.
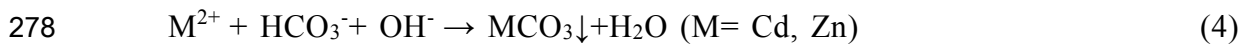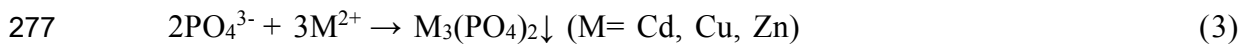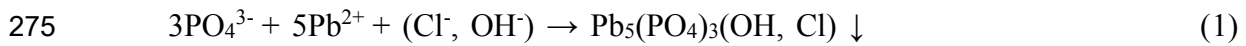
237   *4.1 Heavy metals*

238   An increasing number of studies have shown that both carbon and mineral

239   fractions of biochar can contribute to immobilization of heavy metals (Qian & Chen,

240   2013; Qian et al., 2016). For biochars with a low mineral content, including some crop

241 residue biochars, the sorption of heavy metals occurs mainly through the formation of

242 surface complexes between heavy metals and organic O-containing functional groups

243 (e.g., -COOH, alcoholic -OH or phenolic -OH) on biochar (Tong et al., 2011). However,

244 for biochars rich in minerals, such as manure biochar and sludge biochar, interactions

245 between heavy metals and mineral components may be the dominant factor in sorption

246 (Cao et al., 2009; Lu et al., 2012; Zhang et al., 2013b). Minerals could be responsible

247 for up to 90% of metal removal by biochars (Wang et al., 2015; Xu et al., 2014). Four

248 different possible mechanisms of heavy metal removal by biochar are summarized here

249 and schematically shown in Fig. 2a: (i) electrostatic attraction between cationic (or

250 anionic) metals and negatively (or positively) charged minerals; (ii) cation exchange

251 between metal ions and mineral ions (e.g., K^+, Na^+, Ca^{2+}, and Mg^{2+}) associated with

252 surface functional groups of biochar or present in the biochar; (iii) co-precipitation and

253 inner-sphere complexation of metals with mineral oxides of the biochar; and (iv)

254 precipitation of heavy metals with anions released from minerals (e.g., OH^-, CO_3^{2-},

255 PO_4^{3-}, SO_4^{2-} and SiO_4^{4-}).

256   Various precipitates can be formed during the sorption of heavy metals by different

257 mineral-containing biochars (Table 2). Lead carbonates (e.g., $PbCO_3$ and

258 $Pb_3(CO_3)_2(OH)_2$) and lead phosphates (e.g., $Pb_5(PO_4)_3(OH, Cl)$ and $Pb_9(PO_4)_6$) are the

259 most common precipitates formed in the sorption of Pb by biochars (Inyang et al., 2012;

260 Yin et al., 2016) (Table 2). The possible precipitation reactions have been proposed and

261 are shown below (Cao et al., 2009; Xu et al., 2013) (Reactions 1-2). Apart from these

262 two types of precipitates, new mineral precipitates, e.g., $Pb_2(SO_4)O$,

263 $Pb_4(CO_3)_2(SO_4)(OH)_2$ (Wang et al., 2015), and $PbO \cdot P_2O_5 \cdot SiO_2$ (Lu et al., 2012), were

264 also found during the sorption of Pb^{2+} by biochars. Like Pb, carbonate and phosphate

265 precipitates were found in the sorption of Cd (Trakal et al., 2016), Cu (Arán et al., 2016;

266   Ippolito et al., 2012b), and Zn (Betts et al., 2013; Wagner et al., 2015) by biochars

267   (Table 2). Reactions 3-5 are the possible precipitation reactions that have been proposed

268   (Xu et al., 2013). Additionally, oxide precipitates (e.g., CdO and ZnO) were also

269   observed by Bogusz et al. (2015). Meng et al. (2014) reported that silicate particles

270   within the biochars served as adsorption sites for Cu(II), and $CuSiO_3$ was the final

271   product. Co-precipitation of silicate particles with Al (as $KAlSi_3O_8$) was also observed

272   by Qian and Chen (2013). The sorption of Hg can occur by its precipitation as $HgCl_2$,

273   HgO, or HgS on alkaline biochar surfaces containing high chloride or sulfur contents

274   (Liu et al., 2016).

275        $3PO_4^{3-} + 5Pb^{2+} + (Cl^-, OH^-) \rightarrow Pb_5(PO_4)_3(OH, Cl) \downarrow$ (1)

276        $3Pb^{2+} + 2\ HCO_3^- + 4OH^- \rightarrow Pb_3(CO_3)_2(OH)_2 \downarrow + 2H_2O$ (2)

277        $2PO_4^{3-} + 3M^{2+} \rightarrow M_3(PO_4)_2 \downarrow$ (M= Cd, Cu, Zn)   (3)

278        $M^{2+} + HCO_3^- + OH^- \rightarrow MCO_3 \downarrow + H_2O$ (M= Cd, Zn)   (4)

279        $3Cu^{2+} + 2HCO_3^- + 4OH^- \rightarrow Cu_3(CO_3)_2(OH)_2 \downarrow + 2H_2O$ (5)

280   The precipitation of oxyanionic metals, such as As and Cr, with biochar minerals

281   has rarely been reported and is greatly influenced by their valence state (Chen et al.,

282   2015; Yin et al., 2016). For example, Cr(III) is much easier to stabilize than Cr(VI) and

283   can precipitate as $Cr(OH)_3$ during sorption (Chen et al., 2015). The sorption of Cr (VI)

284   may be enhanced by biochar minerals such as alkaline metals (Shen et al., 2012), but

285   there is limited evidence of the formation of precipitates between them. This is because

286   Cr(VI) is removed by reduction to Cr(III) by the functional groups of biochar (Dong et

287   al., 2011). It was reported that $Ca_5(AsO_4)_3OH$ and $Ca_4(OH)_2(AsO_4)_2(H_2O)_4$ were found

288   in the sorption of As (V) by biochar derived from water hyacinth (Yin et al., 2016). Note

289   that both soluble and insoluble minerals of biochar play important roles in the sorption

290   of heavy metals, but the adsorption affinity of water-soluble fractions is much higher

291 than that of water-insoluble minerals (Xu & Chen, 2014). The solubility of minerals

292 could also influence the sorption kinetics of heavy metals. Since metal removal was

293 mainly attributed to the precipitation of heavy metals by anions (e.g., PO_4^{3-} and CO_3^{2-})

294 released from minerals in biochars, the sorption rate was controlled by the dissolution of

295 the minerals (Wang et al., 2015). In low-temperature biochar, the minerals were

296 amorphous, more soluble, and easier to release for subsequent precipitation with heavy

297 metals (Zheng et al., 2013). On the other hand, in high-temperature biochar, the

298 minerals were more crystallized, less soluble, and more difficult to release (Cao &

299 Harris, 2010). Uchimiya et al. (2012) and Cao et al. (2009) reported that the dairy

300 manure biochar produced at higher temperatures (>500 °C) had a lower content of

301 soluble P due to the association of stable P-Ca-Mg, which was not favorable for the

302 release of P and its subsequent precipitation with Pb. Therefore, the sorption kinetics of

303 biochar produced at low temperatures is faster than that of biochar produced at high

304 temperatures.

305   Cation exchange between biochar mineral elements and heavy metals is also an

306 important mechanism for metal removal. Uchimiya et al. (2010) suggested that as the

307 degree of biochar carbonization and loading of chars increases, heavy metal

308 immobilization by cation exchange becomes increasingly outweighed by other

309 controlling factors, such as the coordination by π electrons (C=C) of carbon and

310 precipitation. The solubility of minerals in the biochar also influences the cation

311 exchange ability. Therefore, biochar produced at a low pyrolysis temperature is

312 favorable for immobilizing heavy metals due to the large release of available mineral

313 components, such as K and Ca, as well as a low degree of carbonization (Uchimiya et

314 al., 2012).

315   The higher the negative charge of the surface, the more pronounced is the

316   electrostatic adsorption of heavy metals. Biochar surface charges depend not only on

317   surface functional groups but also on mineral components (Zhao et al., 2015). Biochar

318   rich in SiO_2 is negatively charged, even at lower pH values (pH <3.0), due to its low

319   isoelectric point (~2.0). Therefore, adsorption of heavy metal ions still occurs, even in

320   low pH ranges (1.5~3.0), by electrostatic adsorption on the SiO_2 components (Xu &

321   Chen, 2014).

322   Since minerals play an important role in the sorption of heavy metals, the sorption

323   efficiency is dramatically reduced after biochar is demineralized or de-ashed. Thus,

324   attempts have been made to increase the sorption capacity of biochar by adding

325   minerals to it. For example, Mn-oxide-modified and birnessite-modified biochars were

326   prepared for the purpose of improving the sorption abilities for As^{3+}, Pb^{2+}, and Cu^{2+}

327   (Song et al., 2014). However, not all minerals are equally effective or favorable for the

328   removal of heavy metals by biochars, and mineral-rich biochars should be used with

329   caution.

330   *4.2. Organic contaminants*

331   Compared to heavy metals, much less work has been done to study the impact of

332   minerals on the sorption of organic contaminants by biochar. However, the presence of

333   minerals has been found to have at least an indirect influence on the sorption of organic

334   contaminants by biochar (Smernik, 2009). For example, minerals may influence the

335   spatial arrangement of organic matter within biochars or the formation of aromatic

336   structures during pyrolysis, and thus affect the sorption behavior of biochar (Smernik,

337   2009; Sun et al., 2013). Additionally, the significantly different sorption performances

338   of biochar before and after mineral removal indicate that minerals could directly

339   influence the sorption of organic contaminants by biochar (Sun et al., 2013). Since the

340　specific type of contaminant can impact the sorption properties of biochar, different

341　minerals might exhibit different effects towards these contaminants.

342　　　The ability of biochar to sorb hydrophobic organic contaminants (HOCs) is closely

343　related to the surface and bulk properties of its carbon fraction, including the graphene-

344　like carbon fraction and the non-crystalline amorphous carbon fraction in biochar. Pore-

345　filling, partitioning, hydrophobicity, aromatic-π interactions, etc. have been proposed as

346　key sorption mechanisms (Zhang et al., 2013a). Therefore, to date, most sorption studies

347　for HOCs have used carbon-rich and low-mineral biochars produced from relatively

348　pure plant residues. In addition, many studies have proven that the presence of minerals

349　is not favorable for the sorption of HOCs. Thus, high-mineral biochars are de-ashed or

350　de-mineralized using acid/alkaline and/or water rinses prior to their use for HOC-

351　sorption. For example, Sun et al. (2013) reported that the organic carbon (OC)-

352　normalized distribution coefficients (Koc) of phenanthrene by biochars generally

353　increased after de-ashing, likely due to the enhancement of favorable and hydrophobic

354　sorption sites by the removal of minerals. Zhang et al. (2013a) stated that the adsorption

355　of carbaryl and atrazine increased greatly after biochar was de-ashed, as the removal of

356　mineral compounds unblocked previously inaccessible organic adsorption sites in the

357　original biochars. De-mineralization and de-ashing treatments can greatly influence the

358　composition and surface characteristics of the biochar, and thus significantly improve

359　the adsorption properties of biochar (Tan et al., 2015).

360　　　On the other hand, the hydrolysis and reduction of hydrophobic organic

361　contaminants could be enhanced with the presence of minerals. For example, Zhang et

362　al (2013a) showed that hydrolysis of carbaryl and atrazine was enhanced due to the

363　catalytic effects of elevated pH, solid mineral surface, and the released dissolved metal

364　ions. The effects of mineral surface on pesticide hydrolysis may include the following

16

365   mechanisms: (1) bound metal atoms present at mineral surface may coordinate a

366   hydrolysable moiety by forming complexes with pesticides, facilitating the nucleophilic

367   attack of water molecules; (2) hydroxo groups bound to the surface may act directly as

368   nucleophiles; and (3) adsorption on the surface (or in vicinal water surrounding the

369   surface) leads to accumulation of reactants (organic compounds and nucleophiles), thus

370   facilitating the reaction (2013a). Biochars may release metal ions into solution, which

371   can catalyze hydrolysis via similar mechanisms as a mineral surface: metal species may

372   facilitate the attack of a nucleophile, analogous to proton catalysis; dissociation of a

373   leaving group may be promoted by interaction of the leaving group with a metal center;

374   a nucleophile bound to metal centers (metal hydroxo species) may have a higher

375   nucleophilicity as compared to its nucleophilicity in bulk water (2013a). Oh et al.

376   (2013) stated that wastewater solids or poultry litter-derived biochars with high contents

377   of redox-active metals, such as Fe, Cu, and Mn, could possibility be involved in the

378   enhanced reduction of nitro herbicides. Although minerals can enhance the abiotic

379   degradation of hydrophobic organic contaminants (e.g. pesticides) via hydrolysis and

380   reduction, it inhibits the non-specific adsorption of organic moieties by reducing the

381   accessibility of organic sorption sites to a larger extent. Therefore, de-mineralization

382   and de-ashing treatments of biochars are still needed for the sorption of hydrophobic

383   organic contaminants.

384   Additionally, some studies have reported that minerals in biochar can enhance the

385   sorption of organic contaminants, especially polar and ionic organic compounds (Xu et

386   al., 2011). This can be ascribed to the following mechanisms: (1) cation-π interactions

387   between organic contaminants and minerals in the biochar; (2) electrostatic attraction

388   between cationic (or anionic) organic contaminants and negatively (or positively)

389   charged minerals; (3) surface complexation (such as H-bonding) between hydroxyl sites

390 on the mineral surface and carboxyl groups on the organic contaminants; and (4) ion

391 exchange reactions. Ji et al. (2011) proved that the mineral fraction played an important

392 role in the tetracycline adsorption by crop residue-derived biochar, due to strong surface

393 complexation of tetracycline with the mineral components via surface complexation

394 (such as H-bonding) and/or ion exchange reactions.

395   As illustrated in Fig. 2b, different minerals have different impacts on the sorption

396 of various types of organic contaminants, such as polar and non-polar, and ionic and

397 non-ionic organic contaminants, by biochar. Therefore, biochars with the appropriate

398 mineral contents and species should be chosen for the removal of specific contaminants.

399 Research on interactions between biochar mineral matter and organic contaminants is

400 needed to provide such reliable prescriptions.

401 *4.3. N and P*

402   In addition to being a potentially important sorbent for organic pollutants and

403 heavy metals, biochar can also act as a potential sorbent for recovering nutrients (NH_4^+

404 and PO_4^{3-}) (Sarkhot et al., 2013). Generally, the surfaces of most carbon-rich and low-

405 mineral biochars are negatively charged and have little or no ability to remove anions,

406 particularly PO_4^{3-} (Jung et al., 2015; Yao et al., 2011). For example, Jung et al. (2015)

407 discovered that biochars derived from soybean stover, bamboo wood, and maize residue

408 showed no sorption capacity for PO_4^{3-} removal and even released inherent PO_4^{3-} into the

409 solution. However, Sarkhot et al. (2013) found that biochar produced from mixed

410 hardwood could effectively sorb PO_4^{3-} via exchange with its surface hydroxyl groups.

411   Compared to low-mineral biochar, biochars with high mineral content, mainly Ca

412 and Mg, usually show a higher capability to sorb phosphate. This sorption ability is

413 associated with the concentration and accessibility of cations found in the mineral

414   fraction of biochar. If Ca is released from the biochars into solution as free ions, they

415   may remove PO_4^{3-} through precipitation. Streubel et al. (2012) reported that co-

416   precipitation as Ca-phosphates was the main mechanism for PO_4^{3-} removal in dairy

417   lagoons by biochar produced from anaerobically digested fiber. Further improvements

418   can be achieved by enriching biochar with certain minerals; for example, Mg-biochar

419   synthesized from Mg-enriched plant tissues was found to be a strong sorbent for P in

420   aqueous media (Yao et al., 2013; Yao et al., 2011). Mg-enriched tomato tissues (Yao et

421   al., 2013), anaerobically digested biomass (Yao et al., 2011), $MgCl_2$-pretreated biomass

422   (Zhang et al., 2012), and other Mg-rich biomass could be used to produce Mg-biochar

423   nanocomposites by pyrolysis. The Mg-enriched biochar contained nanosized MgO and

424    $Mg(OH)_2$ particles within the biochar matrix. The points of zero charge of $Mg(OH)_2$ and

425   MgO are higher than 12, and thus the surfaces of Mg-biochar composites may be

426   positively charged in most natural aqueous solutions with pH < 7. This facilitates

427   electrostatic interactions between negatively charged PO_4^{3-} and biochar surfaces (Yao et

428   al., 2013; Zhang et al., 2012). In addition to Mg oxide, Fe oxide may also enhance the

429   sorption of P by biochar due to inner-sphere complexation on the surface (Li et al.,

430   2016).

431   The ability of biochar to sorb NH_4^+-N is likely due to synergistic interactions

432   among SSA, CEC, and surface functional groups and the release potential of P, Mg, etc.

433   (Kizito et al., 2015; Zhang & Wang, 2016). Kizito et al. (2015) found that chemisorption

434   involving ionic bond formation with surface functional groups and surface-area-

435   dependent physical sorption were the most likely mechanisms of NH_4^+ adsorption. On

436   the other hand, Sarkhot et al. (2013) observed a relatively high degree of correlation

437   between the amount of sorbed NH_4^+ and the amount of cations released by biochar,

438   especially Ca^{2+} ($R^2 = 0.65$), indicating that cation exchange between Ca^{2+} in the biochar
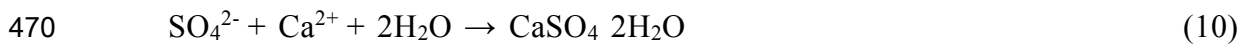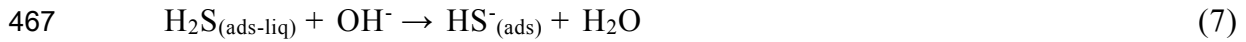
439 and NH_4^+ was the likely mechanism for NH_4^+ adsorption.

440   In conclusion, minerals, especially Ca and Mg, play an important role in the

441 sorption of NH_4^+ and PO_4^{3-} by biochar via precipitation, cation exchange, and

442 electrostatic interactions. Biochar with high contents of Ca and Mg could act as a

443 sorbent for nutrients (NH_4^+ and PO_4^{3-}). The nutrient-enriched biochar obtained after

444 sorption can be used as a slow-release fertilizer in horticulture and agriculture.

445 *4.4. Acidic gas*

446   Biochars with high contents of alkali and alkaline earth metals (K, Ca and Mg,

447 etc.) are often highly alkaline, which favors dissolution of acidic gases, such as SO_2,

448 H_2S, and CO_2, and consequently enhances the removal of these acidic gases. Shang et

449 al. (2013) reported that biochars produced from a series of agricultural/forestry residues,

450 such as rice hull, camphor, bamboo, and rice hull, were effective for the sorption of H_2S.

451 They attributed the sorption ability to the high local pH within the pore systems of these

452 biochars. Some mineral oxides, such as zinc and iron oxides, present in biochars might

453 be effective oxidants for the removal of H_2S (Azargohar & Dalai, 2011). Xu et al.

454 (2016b) stated that the carbon fraction of biochar could catalyze the conversion of H_2S

455 to elemental S^0 and $S(VI)$ (Reactions 6-9), while the minerals could further react with

456 the produced SO_4^{2-}, forming $CaSO_4$ precipitate (Reaction 10) in the sewage sludge

457 biochar and $(K, Na)_2SO_4$ in the pig manure biochar. In addition to H_2S, SO_2 could also

458 be effectively removed by biochar derived from dairy manure, sludge, and rice husk, as

459 reported by Xu et al. (2016b). In their work, $CaCO_3$ and $Ca_3(PO_4)_2$ in dairy-manure

460 biochar induced the conversion of the sorbed SO_2 into $K_2CaSO_4 \cdot H_2O$ and $CaSO_4 \cdot 2H_2O$;

461 in sludge biochar, the sorbed SO_2 was converted to $Fe_2(SO_4)_3 \cdot H_2SO_4 \cdot 2H_2O$,

462 $CaSO_4 \cdot 2H_2O$, and $Ca_3(SO_3)_2SO_4 \cdot 12H_2O$. $K_3H(SO_4)_2$ might exist in the exhausted

463   samples of rice-husk biochar. The chemical transformation of SO_2, induced by inherent

464   mineral components, accounts for 44.6%-85.5% of the SO_2 sorption by biochar (Xu et

465   al., 2016b).

466    $$H_2S_{(gas)} \rightarrow H_2S_{(ads)} \rightarrow H_2S_{(ads-liq)} \tag{6}$$

467    $$H_2S_{(ads-liq)} + OH^- \rightarrow HS^-_{(ads)} + H_2O \tag{7}$$

468    $$HS^-_{(ads)} + O_2 \rightarrow S^0 \tag{8}$$

469    $$HS^-_{(ads)} + O_2 + H_2O \rightarrow SO_4^{2-} \tag{9}$$

470    $$SO_4^{2-} + Ca^{2+} + 2H_2O \rightarrow CaSO_4\ 2H_2O \tag{10}$$

471   Mineral components, such as Mg, Ca, Fe, K, etc., in biochar may convert sorbed

472   CO_2 to bicarbonate/carbonate (Xu et al., 2016b). In order to determine the role of

473   mineral components in the sorption of CO_2 by biochar, Xu et al (2016b) separated the

474   minerals from biochars and used them for CO_2 sorption. XRD analysis of minerals after

475   CO_2 sorption showed that the sorbed CO_2 was transformed to $K_2Ca(CO_3)_2$ and

476    $CaMg(CO_3)_2$ by pig-manure biochar minerals (Fig. S1a), and to $CaMg(CO_3)_2$ by wheat-

477   straw biochar minerals (Fig. S1b).

478   Since minerals in biochar could enhance the capture of acidic gases, impregnation

479   of minerals, such as magnesium hydroxide and iron oxide, into biochar has been used

480   by some authors to improve the performance of original biochars (Creamer et al., 2016).

481   However, the application of biochar for the sorption of acidic gases is still in its infancy

482   and needs further investigation.

483   **5. Effect of minerals on carbon loss and carbon stability**

484   The "biochar" concept was initially developed for dealing with the challenges of

485   climate change caused by the greenhouse effect. It has been proposed that the relatively

486   unstable carbon in biomass can be turned into highly recalcitrant carbon in the form of

487   biochar through pyrolysis, thus achieving atmospheric carbon sequestration (Lehmann,

488   2007). Recently, minerals have been found to enhance the carbon retention and stability

489   of the solid product (biochar) of biomass pyrolysis for carbon sequestration. It has been

490   reported that minerals could catalyze several thermal reactions and greatly alter the

491   product distribution and composition during pyrolysis (Shi et al., 2012). Guo and Chen

492   (2014) reported that Si plays an important role in the arrangement and structural

493   composition of carbon in biochar derived from pyrolysis of rice straw. Si may blend

494   with carbon to form Si-encapsulated carbon with a dense structure, increasing the

495   stability of the biochar. The authors also noted that this possible protection by Si-

496   encapsulation was regulated by pyrolysis temperatures (Guo & Chen, 2014). Apart from

497   Si, P is also considered to be an effective mineral element for increasing carbon

498   retention in biochar during pyrolysis and for increasing its recalcitrance. Li et al. (2014)

499   and Zhao et al. (2016) reported that co-pyrolysis of waste biomass with a P mineral (e.g.

500    $Ca(H_2PO_4)_2$) could reduce carbon loss during pyrolysis (Fig. 3a) and enhance its

501   stability against chemical oxidation (Fig. 3b) and microbial mineralization (Fig. 3c).

502   Enhanced formation of aromatic C, C-O-P, or C-P were speculated to be the main

503   causes behind these effects. Li et al. (2014) also found that kaolin and $CaCO_3$ had little

504   effect on carbon retention in biochar (Fig. 3b and 3c). Hence, the effect of minerals on

505   biochar-C retention and stability depends upon the mineral type, mineral quantity,

506   feedstock type, and pyrolysis conditions. However, reports on this aspect are fairly

507   limited and further research is needed.

508   **6. Effect of minerals on nutrient value of biochar**

509   Many studies have reported that biochar can be used for soil amendment to

510   improve soil quality and increase crop production. In this regard, an obviously positive

22

511   attribute of biochar is its nutrient value, supplied either directly by providing nutrients

512   to plants or indirectly by improving the soil quality. Since the details on soil are out of

513   scope of Bioresource Technology, this section is only shown in Supporting Information.

514   **7. Effect of minerals on other applications of biochar**

515   In addition to the fields discussed in the previous sections, minerals may also play

516   an important role in other applications, including fuel cell precursors, supercapacitors,

517   or as photoactive components. It has been reported that sludge biochar has a very high

518   catalytic activity for the Oxygen Reduction Reaction (ORR) in a microbial fuel cell.

519   Here, a high surface area and the higher N and Fe contents of biochar might have jointly

520   contributed to the high catalytic activity (Yuan et al., 2013). Ahn et al. (2013)

521   investigated the utilization of wood biochar in the direct carbon fuel cell (DCFC)

522   system and found that the performance of this higher ash biochar could reach 60–70%

523   of that of coal. However, the role of minerals in the DCFC system was not fully

524   elucidated, and the author attributed the potential of biomass char as a DCFC fuel to its

525   porous characteristics and the functional groups on the char surface (Ahn et al., 2013).

526   Another area where biochar has gained a foothold is in the production of electrodes for

527   supercapacitors, which are essential electric devices for energy storage (Kai et al.,

528   2015). Although the minerals might not favor the capacitive performance of biochar

529   capacitor following the electric double-layer mechanism (Abioye & Ani, 2015), the

530   capacitor containing metal hydroxides, transition metal oxides could have a great

531   pseudo-capacitive ability (Wang et al., 2017). Wang et al (2017) found that Ni-rich

532   biochar could be converted into supercapacitors with both pseudo-capacitive and

533   electric double-layer properties. They attributed the increase of capacitance in the Ni-

534   rich biochar supercapacitor to the existence of NiO and NiOOH (Wang et al., 2017). In

535   addition to applications in fuel cells and supercapacitors, Fu et al. (2015) noted that

536   dissolved black carbon released from biochar can be one of the more photoactive

537   components in the dissolved organic matter (DOM) pool, and silica minerals in

538   dissolved biochar could mediate electron transfer reactions that are responsible for the

539   generation of superoxide.

540   From the above discussion, it is clear that biochar has various conventional and

541   emerging applications, in which inherent minerals play a variety of roles. A thorough

542   understanding of the role of biochar-bound minerals in different applications will allow

543   the design or selection of the most suitable biochar, with minerals appropriate for

544   specific applications. Table 3 summarizes the preferred minerals addition to the

545   designed biochar for specific applications. Production and application of the designed

546   biochar with mineral incorporation has a great research prospect which will be our

547   future study.

548   **8. Conclusions**

549   The biochar-inherent minerals have the potential to influence its physicochemical

550   properties and its performance in different applications. However, the understanding of

551   the role of mineral components in biochar is fairly limited, and greater efforts must be

552   made across many areas, such as (1) the bioavailability of toxic metals contained in

553   certain types of biochar; (2) the role of biochar-inherent minerals in carbon

554   sequestration and other emerging applications, e.g., as a precursor of catalysts and

555   photoactive components; and (3) design of biochar for specific applications by

556   incorporating appropriate minerals into feedstock or biochar.

557

558   **Supporting Information**

559 Supplementary data associated with this article can be found in the online version.

560

561 **Acknowledgement**

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839 **Figure captions**

840 **Fig. 1.** Relationship between ash (mineral) content and carbon content (a), pH (b), and

841 pore structure (c).

842 **Fig. 2.** Mineral-components related mechanisms of biochar for removal of heavy

843 metal (a) and organic contaminant (b).

844 **Fig. 3.** Phosphate mineral reduced the weight loss of biomass during pyrolysis (a),

845 carbon loss of biochar through chemical oxidation (b), and cumulative CO_2 emission

846 under aerobiotic condition during 60-d incubation period (c), compared to original

847 biochar without phosphate addition (Li et al., 2014; Zhao et al., 2016).

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Table 1

Mineral constituents profile of biochar derived from different feedstock and pyrolysis temperature.

Feedstock		Temperature (°C)	Total inorganic component (%)					Dissolved inorganic component (mg kg⁻¹)					Reference
			N	P	K	Ca	Mg	N	P	K	Ca	Mg	
Plant residues	Corncob	500	2.05	0.08	3.67	0.27	0.06	/	100	10,376	5	9	Zhao et al. (2013)
	Peanut shell	500	2.56	0.17	1.73	1.34	0.46	/	24	1,863	26	28	Zhao et al. (2013)
	Pollyseed hull	500	1.35	0.13	3.25	0.36	0.23	2	80	6,893	46	59	Zhao et al. (2013)
	Rice husk	500	1.23	0.12	0.68	0.13	0.06	/	376	1,370	28	95	Zhao et al. (2013)
	Rice straw	500	1.58	0.24	4.09	1.16	0.34	/	211	13,519	8	16	Zhao et al. (2013)
	Wheat straw	200	/	0.02	1.55	0.29	0.09	/	/	/	/	/	Zhao et al. (2013)
	Wheat straw	350	/	0.04	2.94	0.54	0.19	/	/	/	/	/	Zhao et al. (2013)
	Wheat straw	500	1.58	0.07	5.18	0.95	0.30	13	211	13,519	8	16	Zhao et al. (2013)
	Wheat straw	650		0.08	5.75	1.06	0.33	/	/	/	/	/	Zhao et al. (2013)
	Wheat straw	400	/	/	/	/	/	/	/	10200	242	89	Kloss et al. (2012)
	Wheat straw	460	/	/	/	/	/	/	/	13500	709	212	Kloss et al. (2012)
	Wheat straw	525	/	/	/	/	/	/	/	18200	187	36	Kloss et al. (2012)
	Bagasse	600	0.26	0.08	0.74	0.76	0.15	/	35	1,970	430	130	Wu et al. (2016)
	Peanut hull	600	2.12	0.19	0.93	0.56	0.23	/	170	3,500	520	140	Wu et al. (2016)
	Hickory woodchips	600	0.13	0.04	0.34	0.59	0.16	/	12	1,170	200	73	Wu et al. (2016)
	Pine needle	600	0.67	0.11	0.14	0.68	0.11	/	93	340	540	93	Wu et al. (2016)
	Hardwood	400	0.25	0.02	0.30	0.57	0.07	1	12	1,135	/	/	Tian et al. (2016)
	Hardwood	500	0.30	0.03	0.36	0.71	0.09	/	6	1,096	/	/	Tian et al. (2016)
Manure	Chicken manure	500	2.13	1.94	1.72	5.40	0.51	/	/	/	/	/	Meier et al. (2015)

Chicken manure	500	1.62	0.88	1.44	4.28	0.75	6	100	5,325	66	39	Zhao et al. (2013b)
Cow manure	500	1.99	0.65	1.02	3.80	1.57	31	33	874	55	29	Zhao et al. (2013b)
Pig manure	500	2.32	4.39	3.56	3.47	2.80	8	1919	2,556	2	254	Zhao et al. (2013b)
Mixed animal waste	600	1.14	0.99	3.70	1.96	0.62	/	901	7,100	490	51	Wu et al. (2016)
Poultry litter	400	3.90	2.63	5.03	3.98	1.21	/	2561	43,368	294	737	Tian et al. (2016)
Poultry litter	500	3.75	2.95	5.48	4.37	1.36	120	4529	48,009	/	662	Tian et al. (2016)
Poultry litter	400	5.85	2.00	3.88	2.83	1.73	/	/	/	/	/	Subedi et al. (2016)
Poultry litter	600	4.01	2.87	5.88	3.59	2.40	/	/	/	/	/	Subedi et al. (2016)
Swine manure	400	2.23	2.21	1.62	2.03	1.57	/	/	/	/	/	Subedi et al. (2016)
Swine manure	600	1.79	2.82	3.53	2.89	2.13	/	/	/	/	/	Subedi et al. (2016)
Poultry litter	300	4.17	2.27	6.93	7.18	1.86	4910	343	32,010	238	278	Song et al. (2012)
Poultry litter	350	3.22	2.40	7.46	7.64	1.97	3490	138	34,180	199	128	Song et al. (2012)
Poultry litter	400	2.63	2.63	8.12	8.34	2.15	1460	172	36,670	152	65	Song et al. (2012)
Poultry litter	450	2.23	2.66	8.57	8.79	2.28	154	725	39,170	65	56	Song et al. (2012)
Poultry litter	500	1.21	2.79	8.79	9.05	2.33	124	916	40,400	51	50	Song et al. (2012)
Poultry litter	550	0.31	2.98	8.97	9.30	2.38	252	2045	43,890	43	48	Song et al. (2012)
Poultry litter	600	0.12	3.05	9.15	9.40	2.42	331	1916	44,610	38	46	Song et al. (2012)
Poultry litter	400	5.18	0.58	2.49	3.34	0.68	/	/	/	/	/	Singh et al. (2010)
Poultry litter	550	3.79	0.60	2.30	3.99	0.75	/	/	/	/	/	Singh et al. (2010)
Cow manure	400	1.35	0.44	2.64	1.75	1.07	/	/	/	/	/	Singh et al. (2010)
Cow manure	550	1.14	0.49	2.31	1.88	1.18	/	/	/	/	/	Singh et al. (2010)
Poultry manure	250	/	1.86	4.97	5.76	1.14	/	82	8,288	378	166	Gunes et al. (2015)
Poultry manure	300	/	2.06	5.35	6.53	1.25	/	6	8,963	461	102	Gunes et al. (2015)
Poultry manure	350	/	2.35	6.45	7.57	1.50	/	4	8,568	211	28	Gunes et al. (2015)

	Poultry manure	400	/	2.55	7.01	8.67	1.76	/	6	8,012	259	21	Gunes et al. (2015)
Sludge	Sewage sludge	300	6.12	3.88	0.75	2.06	0.62	2528	280	1,236	/	/	Yuan et al. (2015)
	Sewage sludge	400	3.79	4.27	0.90	2.27	0.70	2544	316	1,032	/	/	Yuan et al. (2015)
	Sewage sludge	500	1.85	4.47	1.01	2.39	0.75	2264	512	736	/	/	Yuan et al. (2015)
	Sewage sludge	600	1.46	4.51	1.33	2.40	0.79	1724	532	340	/	/	Yuan et al. (2015)
	Sewage sludge	700	0.91	4.92	1.66	2.58	0.81	1540	676	316	/	/	Yuan et al. (2015)
	Sewage sludge	300	3.40	2.95	0.16	1.16	1.10	/	/	/	/	/	Lu et al. (2013)
	Sewage sludge	400	2.80	2.92	0.20	1.19	1.34	/	/	/	/	/	Lu et al. (2013)
	Sewage sludge	500	2.30	3.41	0.22	1.22	1.25	/	/	/	/	/	Lu et al. (2013)
	Sewage sludge	600	2.00	3.55	0.26	1.46	1.45	/	/	/	/	/	Lu et al. (2013)
	Sewage sludge	300	6.17	1.04	0.23	0.53	0.14	1000	730	510	530	250	Zhang et al. (2015)
	Sewage sludge	400	4.96	1.16	0.25	0.56	0.14	210	150	490	210	200	Zhang et al. (2015)
	Sewage sludge	500	4.32	1.66	0.28	0.60	0.17	/	170	470	180	180	Zhang et al. (2015)
	Sewage sludge	600	3.54	1.82	0.28	0.65	0.22	/	150	870	/	180	Zhang et al. (2015)
	Sewage sludge	700	3.08	2.00	0.29	0.78	0.26	/	110	1,280	/	180	Zhang et al. (2015)
	Sewage sludge	800	2.50	1.90	0.34	0.86	0.29	/	160	1,410	/	180	Zhang et al. (2015)
	Sewage sludge	900	1.24	1.95	0.34	0.91	0.32	/	260	500	/	170	Zhang et al. (2015)
	Wastewater sludge	500	2.86	1.70	0.53	6.57	0.65	73	2	156	1154	62	Zhao et al. (2013b)

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Table 2

Possible precipitates formed during the sorption of heavy metals by different biochars

Heavy Metals	Feedstock	Pyrolysis temperature (°C)	Possible precipitates	Reference
Pb	Alternanthera philoxeroides	600	$PbCO_3$, $Pb_3(CO_3)_2(OH)_2$	Yu et al. (2014)
	Dairy manure	350/450/500	$Pb_5(PO_4)_3(OH, Cl)$, $Pb_9(PO_4)_6$, $Pb_3(CO_3)_2(OH)_2$, $PbCO_3$	Cao et al. (2009), Xu et al (2013)
	Digested sugar beet/Sugarcane bagasse	600	$Pb_3(CO_3)_2(OH)_2$	Inyang et al. (2012)
	Peanut shell/Medicine residues	300/350/400	$Pb_2(SO_4)O$, $Pb_4(CO_3)_2(SO_4)(OH)_2$	Wang et al. (2015)
	Sludge	550	$PbO·P_2O_5·SiO_2$	Lu et al. (2012)
	Water hyacinth	450	$Pb_5(PO_4)_3OH$, $Pb_5(PO_4)_3Cl$	Yin et al. (2016)
Cd	Dairy manure	350	$Cd_3(PO_4)_2$	Xu et al. (2013)
	Nut shield/plum stone/Grape stalk	600	$CdCO_3$	Trakal et al. (2016)
	Water hyacinth	450	$CdCO_3$, Cd_3P_2, $Cd_3(PO_4)_2$, K_4CdCl_6	Zhang et al. (2015a)
	Wheat straw/S. hermaphrodita	700	CdO	Bogusz et al. (2015)
Cu	Pecan shell	700	$Cu_3(CO_3)_2(OH_2)$, CuO	Ippolito et al. (2012b)
	Rice husk	300-400	$Cu_3(PO_4)_2$	Arán et al. (2016)
	Swine manure	400/700	$CuSiO_3$, $K-Cu-PO_4$, $Ca-Cu-PO_4$	Meng et al. (2014)
	Wheat straw/S. hermaphrodita	700	$Cu_3(CO_3)_2(OH_2)$, Cu_2O	Bogusz et al. (2015)
Zn	Meat and bonemeal	-	$ZnPO_4$	Betts et al. (2013)
	Miscanthus	860	$Zn_3(PO_4)_2$, $Zn_3(PO_4)_2·4H_2O$	Wagner et al. (2015)
	Wheat straw/S. hermaphrodita	700	ZnO	Bogusz et al. (2015)
Hg	Wood/Manure	300/600	$HgCl_2$, $Hg-O$, $Hg-S$	Liu et al. (2016)
Cr	Sewage sludge	900	$Cr(OH)_3$	Chen et al. (2015b)
As	Water hyacinth	450	$Ca_5(AsO_4)_3OH$, $Ca_4(OH)_2(AsO_4)_2(H_2O)_4$	Yin et al. (2016)

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Preferred minerals addition to the designed biochar for different applications.

Biochar applications	Mechanisms	Preferred minerals
Heavy metal removal (Pb, Cu, Zn, Cd, etc.)	Precipitation	Minerals containing OH^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, SiO_4^{4-}, etc.
	Cation exchange	Minerals containing K, Na, Ca, Mg, etc.
	Electrostatic attraction	SiO_2, etc.
Organic pollutant removal (PAH, etc.)	Cation-π interactions	Minerals containing Fe, Mg, Si, K, Ca, etc
	Surface complexation	Minerals containing OH, etc.
PO_4^{3-} removal	Precipitation	Mineral containing Ca, etc.
	Electrostatic attraction	Mg oxide, etc.
	Surface inner-sphere complexation	Fe oxide, etc.
NH_4^+ removal	Cation exchange	Minerals containing K, Na, Ca, Mg, etc.
Acidic gases removal (H_2S, SO_2, CO_2, etc.)	Chemical transformation	Mineral containing Mg, Ca, Fe, K, etc.
Carbon sequestration	Formation of aromatic C, C-O-P, or C-P	Minerals containing P, e.g. $Ca(H_2PO_4)_2$
	Formation of Si-encapsulated carbon	Minerals containing Si
Soil amendment	Direct nutrient release	Plant macro- and micro-nutrients
	Increasing CEC	Minerals containing basic cations, such as K, Na, Ca, Mg
	Liming effect	KOH, NaOH, $MgCO_3$, and $CaCO_3$, etc.
	Improving water-holding capacity	Minerals containing electron-deficient metals, such as Al
	Retention of P	Fe and Al oxides

Fig. 1

(a)

① Precipitation
② Cation exchange
③ Electrostatic attraction
④ Surface complexation

M^{2+}: Heavy metal ions

① Hydrophobic site decreased
② Block the pore
③ Catalytic hydrolysis
④ Oxidation and reduction
⑤ Electrostatic attraction
⑥ Cation-π interactions
⑦ Surface complexation
⑧ Ion exchange reaction

Fig. 2

Fig. 3