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### Indispensable role of biochar-inherent mineral constituents in its environmental applications

**Citation for published version:**

Xu, X, Zhao, Y, Sima, J, Zhao, L, Masek, O & Cao, X 2017, 'Indispensable role of biochar-inherent mineral constituents in its environmental applications', *Bioresource technology*.  
<https://doi.org/10.1016/j.biortech.2017.06.023>

**Digital Object Identifier (DOI):**

[10.1016/j.biortech.2017.06.023](https://doi.org/10.1016/j.biortech.2017.06.023)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

Bioresource technology

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

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1   **Abstract**

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

22

23   *Keywords:* Biochar; Contaminant sorption; Carbon sequestration; Mineral constituents;  
24   Nutrient bioavailability

25     **1. Introduction**

26       Biochar, a carbon-rich byproduct of biomass pyrolysis, is receiving increasing  
27       attention due to its multiple functions in carbon sequestration, reduction of greenhouse  
28       gas emissions, soil improvement, environmental remediation, etc. (Beesley et al., 2011;  
29       Lehmann et al., 2011). It has been commonly assumed that the carbon fraction of  
30       biochar plays a dominant role in its applications (Chen et al., 2008a; Lee et al., 2010).  
31       For example, the stable and rich aromatic forms of the C fraction enable biochar to be  
32       used as a means of sequestering atmospheric CO<sub>2</sub> (Lehmann, 2007); because of its high  
33       organic C content and porous structure, biochar has the potential to serve as a soil  
34       conditioner to improve the physicochemical and biological properties of soils (Ippolito  
35       et al., 2012a); partitioning and adsorption by the carbon fraction of biochar could be  
36       effective sorption mechanisms for organic contaminants (Chen et al., 2008a);  
37       complexation with organic O-containing functional groups, such as -COOH, alcoholic-  
38       OH, or phenolic-OH groups, is involved in heavy-metal sorption by biochars (Lu et al.,  
39       2012).

40       In addition to the rich carbon fraction, biochar often contains high levels of mineral  
41       (ash) components, such as alkali metals (K, Na, etc.) or alkaline earth metals (Ca, Mg,  
42       etc.), which are often present in the form of carbonates, phosphates, or oxides (Cao &  
43       Harris, 2010; Xu et al., 2014). Compared to the carbon fraction, the role of the mineral  
44       fraction in biochar applications has received less attention, probably because (1) the  
45       biomasses used for the generation of biochar are mostly plant residues, which contain  
46       limited mineral components (e.g., woody biomass) (Hale et al., 2016); and (2)  
47       demineralization or de-ashing treatments are often applied to remove the mineral  
48       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<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>, 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**

73 **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 ( $\text{KH}_2\text{PO}_4$ ), chlorocalcite ( $\text{KCaCl}_3$ ), kalicinite ( $\text{KHCO}_3$ ), pyrocoprite  
92    ( $\text{K}_2\text{MgP}_2\text{O}_7$ ), struvite-K ( $\text{KMgPO}_4 \cdot 6 \text{ H}_2\text{O}$ ), and sylvite ( $\text{KCl}$ ). The most common  
93    minerals present in biochars include sylvite ( $\text{KCl}$ ), quartz ( $\text{SiO}_2$ ), amorphous silica,  
94    calcite ( $\text{CaCO}_3$ ), hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ), 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  $\text{PO}_4^{3-}$ -P in peanut-shell-  
112 derived biochar decreased from 430 to 70 mg kg<sup>-1</sup> when the pyrolytic temperature  
113 increased from 300 °C to 600 °C, due to the formation of less soluble crystalline  
114 phosphates, such as  $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{Mg}_2\text{PO}_4\text{OH}$ , 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 ( $\text{MgCO}_3$ ), calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), 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\\_That\\_Is\\_Used\\_in\\_Soil\\_Final.pdf](http://www.biochar-international.org/sites/default/files/Guidelines_for_Biochar_That_Is_Used_in_Soil_Final.pdf)). This IBI classification is based on organic C  
152 rather than the total C. Since the content of organic C in biochar is much larger than  
153 inorganic C, total C is used to represent organic C for the classification in this study.  
154 Figure 1a and Table S1 summarize the negative relationship between the carbon content  
155 and mineral content ( $R^2=0.76$ ), showing that most Class 1 biochars contain less than  
156 20% minerals; Class 2 biochars contain 20%-60% minerals; and the mineral content of  
157 Class 3 biochars is higher than 60%. Therefore, in order to discuss the effect of minerals  
158 on the properties of biochar, we also categorize biochar into three classes, based on the  
159 mineral content. These include: Class 1 biochar (below 20% minerals), Class 2 biochar  
160 (between 20% and 60% minerals), and Class 3 biochar (containing 60% minerals or  
161 more). Note that this classification may not map exactly with the IBI classification, e.g.,  
162 some biochars may have low ash content as well as a low carbon content due to high H,  
163 N, and O contents. However, the carbon content of most biochars is negatively related  
164 to the mineral content ( $R^2=0.76$ ), based on the 278 biochar samples summarized in this  
165 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 ( $\text{pH} > 7.0$ ) (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<sup>+</sup> 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<sup>-</sup> (–COOH) and –O<sup>-</sup> (–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<sub>3</sub>, and CaCO<sub>3</sub> 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<sup>2</sup> g<sup>-1</sup>) and pore volume (PV, up to 1.40 cm<sup>3</sup> g<sup>-1</sup>) than Class 2 and 3  
207 biochars (SA, below 200 m<sup>2</sup> g<sup>-1</sup>; PV, below 0.45 cm<sup>3</sup> g<sup>-1</sup>), 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.

218     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  $\text{SiO}_2$  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.

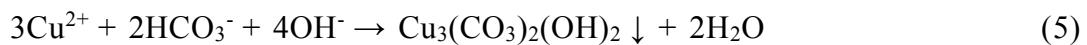
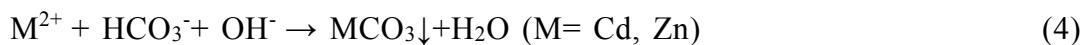
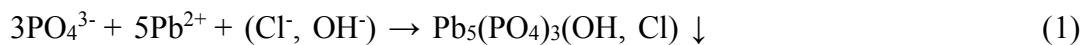
237     *4.1 Heavy metals*

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<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) 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<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>,  
255 PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and SiO<sub>4</sub><sup>4-</sup>).

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<sub>3</sub> and  
258 Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>) and lead phosphates (e.g., Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH, Cl) and Pb<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>) 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<sub>2</sub>(SO<sub>4</sub>)O,  
263 Pb<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>(SO<sub>4</sub>)(OH)<sub>2</sub> (Wang et al., 2015), and PbO·P<sub>2</sub>O<sub>5</sub>·SiO<sub>2</sub> (Lu et al., 2012), were  
264 also found during the sorption of Pb<sup>2+</sup> 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<sub>3</sub> was the final  
271 product. Co-precipitation of silicate particles with Al (as KAlSi<sub>3</sub>O<sub>8</sub>) was also observed  
272 by Qian and Chen (2013). The sorption of Hg can occur by its precipitation as HgCl<sub>2</sub>,  
273 HgO, or HgS on alkaline biochar surfaces containing high chloride or sulfur contents  
274 (Liu et al., 2016).



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)<sub>3</sub> 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<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>OH and Ca<sub>4</sub>(OH)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> 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.,  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$ )  
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  $\pi$  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<sub>2</sub> 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<sub>2</sub> 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<sup>3+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup>  
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- $\pi$  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 ( $K_{oc}$ ) 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

mechanisms: (1) bound metal atoms present at mineral surface may coordinate a hydrolysable moiety by forming complexes with pesticides, facilitating the nucleophilic attack of water molecules; (2) hydroxo groups bound to the surface may act directly as nucleophiles; and (3) adsorption on the surface (or in vicinal water surrounding the surface) leads to accumulation of reactants (organic compounds and nucleophiles), thus facilitating the reaction (2013a). Biochars may release metal ions into solution, which can catalyze hydrolysis via similar mechanisms as a mineral surface: metal species may facilitate the attack of a nucleophile, analogous to proton catalysis; dissociation of a leaving group may be promoted by interaction of the leaving group with a metal center; a nucleophile bound to metal centers (metal hydroxo species) may have a higher nucleophilicity as compared to its nucleophilicity in bulk water (2013a). Oh et al. (2013) stated that wastewater solids or poultry litter-derived biochars with high contents of redox-active metals, such as Fe, Cu, and Mn, could possibly be involved in the enhanced reduction of nitro herbicides. Although minerals can enhance the abiotic degradation of hydrophobic organic contaminants (e.g. pesticides) via hydrolysis and reduction, it inhibits the non-specific adsorption of organic moieties by reducing the accessibility of organic sorption sites to a larger extent. Therefore, de-mineralization and de-ashing treatments of biochars are still needed for the sorption of hydrophobic organic contaminants.

Additionally, some studies have reported that minerals in biochar can enhance the sorption of organic contaminants, especially polar and ionic organic compounds (Xu et al., 2011). This can be ascribed to the following mechanisms: (1) cation- $\pi$  interactions between organic contaminants and minerals in the biochar; (2) electrostatic attraction between cationic (or anionic) organic contaminants and negatively (or positively) 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 ( $\text{NH}_4^+$   
404 and  $\text{PO}_4^{3-}$ ) (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  $\text{PO}_4^{3-}$  (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  $\text{PO}_4^{3-}$  removal and even released inherent  $\text{PO}_4^{3-}$  into the  
409 solution. However, Sarkhot et al. (2013) found that biochar produced from mixed  
410 hardwood could effectively sorb  $\text{PO}_4^{3-}$  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

fraction of biochar. If Ca is released from the biochars into solution as free ions, they may remove  $\text{PO}_4^{3-}$  through precipitation. Streubel et al. (2012) reported that co-precipitation as Ca-phosphates was the main mechanism for  $\text{PO}_4^{3-}$  removal in dairy lagoons by biochar produced from anaerobically digested fiber. Further improvements can be achieved by enriching biochar with certain minerals; for example, Mg-biochar synthesized from Mg-enriched plant tissues was found to be a strong sorbent for P in aqueous media (Yao et al., 2013; Yao et al., 2011). Mg-enriched tomato tissues (Yao et al., 2013), anaerobically digested biomass (Yao et al., 2011),  $\text{MgCl}_2$ -pretreated biomass (Zhang et al., 2012), and other Mg-rich biomass could be used to produce Mg-biochar nanocomposites by pyrolysis. The Mg-enriched biochar contained nanosized  $\text{MgO}$  and  $\text{Mg(OH)}_2$  particles within the biochar matrix. The points of zero charge of  $\text{Mg(OH)}_2$  and  $\text{MgO}$  are higher than 12, and thus the surfaces of Mg-biochar composites may be positively charged in most natural aqueous solutions with  $\text{pH} < 7$ . This facilitates electrostatic interactions between negatively charged  $\text{PO}_4^{3-}$  and biochar surfaces (Yao et al., 2013; Zhang et al., 2012). In addition to Mg oxide, Fe oxide may also enhance the sorption of P by biochar due to inner-sphere complexation on the surface (Li et al., 2016).

The ability of biochar to sorb  $\text{NH}_4^+$ -N is likely due to synergistic interactions among SSA, CEC, and surface functional groups and the release potential of P, Mg, etc. (Kizito et al., 2015; Zhang & Wang, 2016). Kizito et al. (2015) found that chemisorption involving ionic bond formation with surface functional groups and surface-area-dependent physical sorption were the most likely mechanisms of  $\text{NH}_4^+$  adsorption. On the other hand, Sarkhot et al. (2013) observed a relatively high degree of correlation between the amount of sorbed  $\text{NH}_4^+$  and the amount of cations released by biochar, especially  $\text{Ca}^{2+}$  ( $R^2 = 0.65$ ), indicating that cation exchange between  $\text{Ca}^{2+}$  in the biochar

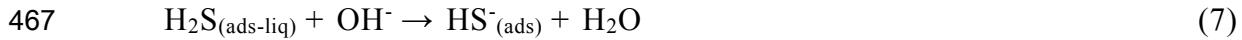
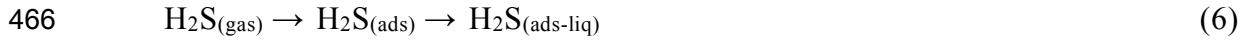
439 and NH<sub>4</sub><sup>+</sup> was the likely mechanism for NH<sub>4</sub><sup>+</sup> adsorption.

440 In conclusion, minerals, especially Ca and Mg, play an important role in the  
441 sorption of NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> 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<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>). 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<sub>2</sub>,  
448 H<sub>2</sub>S, and CO<sub>2</sub>, 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<sub>2</sub>S.  
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<sub>2</sub>S (Azargohar & Dalai, 2011). Xu et al.  
454 (2016b) stated that the carbon fraction of biochar could catalyze the conversion of H<sub>2</sub>S  
455 to elemental S<sup>0</sup> and S(VI) (Reactions 6-9), while the minerals could further react with  
456 the produced SO<sub>4</sub><sup>2-</sup>, forming CaSO<sub>4</sub> precipitate (Reaction 10) in the sewage sludge  
457 biochar and (K, Na)<sub>2</sub>SO<sub>4</sub> in the pig manure biochar. In addition to H<sub>2</sub>S, SO<sub>2</sub> 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<sub>3</sub> and Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> in dairy-manure  
460 biochar induced the conversion of the sorbed SO<sub>2</sub> into K<sub>2</sub>CaSO<sub>4</sub>H<sub>2</sub>O and CaSO<sub>4</sub>2H<sub>2</sub>O;  
461 in sludge biochar, the sorbed SO<sub>2</sub> was converted to Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>H<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O,  
462 CaSO<sub>4</sub>2H<sub>2</sub>O, and Ca<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·12H<sub>2</sub>O. K<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> might exist in the exhausted

463 samples of rice-husk biochar. The chemical transformation of SO<sub>2</sub>, induced by inherent  
464 mineral components, accounts for 44.6%-85.5% of the SO<sub>2</sub> sorption by biochar (Xu et  
465 al., 2016b).



471 Mineral components, such as Mg, Ca, Fe, K, etc., in biochar may convert sorbed  
472 CO<sub>2</sub> to bicarbonate/carbonate (Xu et al., 2016b). In order to determine the role of  
473 mineral components in the sorption of CO<sub>2</sub> by biochar, Xu et al (2016b) separated the  
474 minerals from biochars and used them for CO<sub>2</sub> sorption. XRD analysis of minerals after  
475 CO<sub>2</sub> sorption showed that the sorbed CO<sub>2</sub> was transformed to K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub> and  
476 CaMg(CO<sub>3</sub>)<sub>2</sub> by pig-manure biochar minerals (Fig. S1a), and to CaMg(CO<sub>3</sub>)<sub>2</sub> 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

biochar through pyrolysis, thus achieving atmospheric carbon sequestration (Lehmann, 2007). Recently, minerals have been found to enhance the carbon retention and stability of the solid product (biochar) of biomass pyrolysis for carbon sequestration. It has been reported that minerals could catalyze several thermal reactions and greatly alter the product distribution and composition during pyrolysis (Shi et al., 2012). Guo and Chen (2014) reported that Si plays an important role in the arrangement and structural composition of carbon in biochar derived from pyrolysis of rice straw. Si may blend with carbon to form Si-encapsulated carbon with a dense structure, increasing the stability of the biochar. The authors also noted that this possible protection by Si-encapsulation was regulated by pyrolysis temperatures (Guo & Chen, 2014). Apart from Si, P is also considered to be an effective mineral element for increasing carbon retention in biochar during pyrolysis and for increasing its recalcitrance. Li et al. (2014) and Zhao et al. (2016) reported that co-pyrolysis of waste biomass with a P mineral (e.g.  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ) could reduce carbon loss during pyrolysis (Fig. 3a) and enhance its stability against chemical oxidation (Fig. 3b) and microbial mineralization (Fig. 3c). Enhanced formation of aromatic C, C-O-P, or C-P were speculated to be the main causes behind these effects. Li et al. (2014) also found that kaolin and  $\text{CaCO}_3$  had little effect on carbon retention in biochar (Fig. 3b and 3c). Hence, the effect of minerals on biochar-C retention and stability depends upon the mineral type, mineral quantity, feedstock type, and pyrolysis conditions. However, reports on this aspect are fairly 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

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**

562 This work was supported in part by National Natural Science Foundation of China (No.

563 21537002, 21377081, 21607099) and China Postdoctoral Science Foundation.

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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<sub>2</sub> 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 <sup>-1</sup> )					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)

**Table 2**

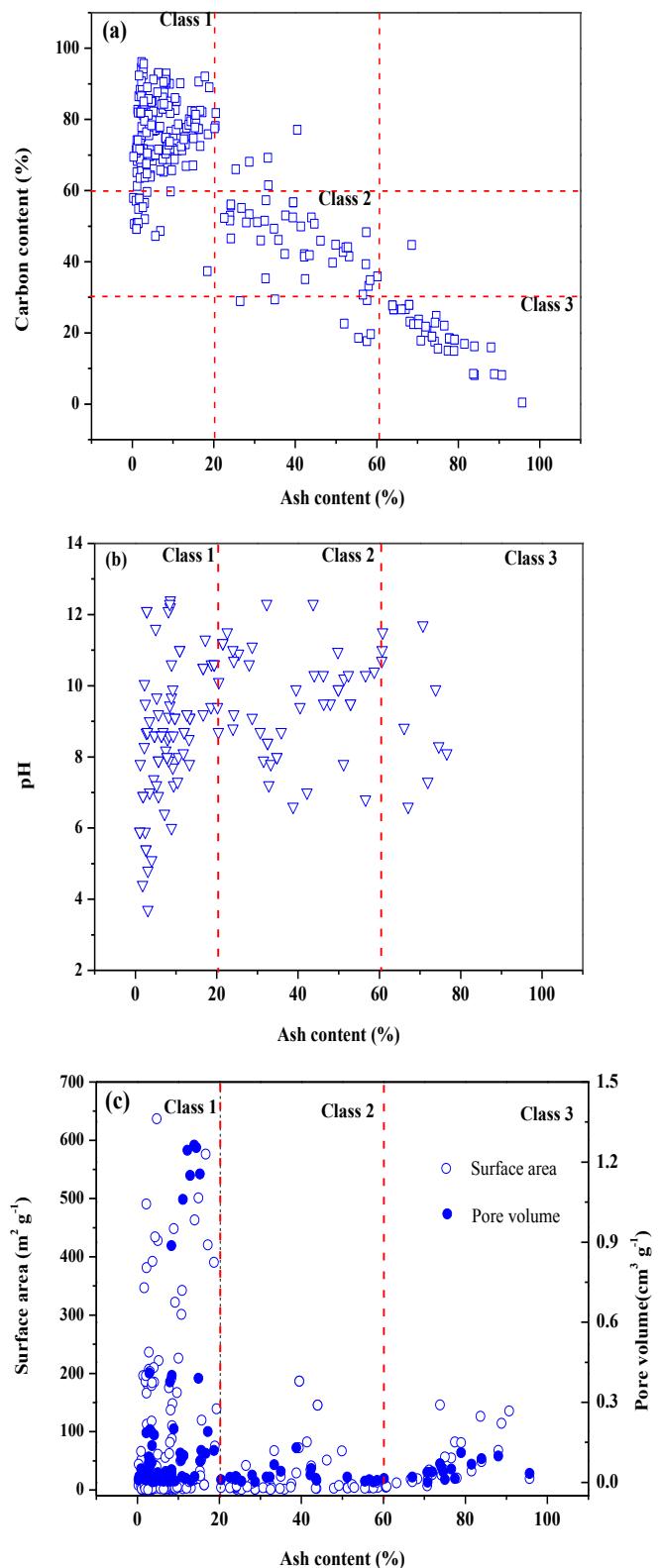
Possible precipitates formed during the sorption of heavy metals by different biochars

Heavy Metals	Feedstock	Pyrolysis temperature (°C)	Possible precipitates	Reference
Pb	Alternanthera philoxeroides	600	PbCO <sub>3</sub> , Pb <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	Yu et al. (2014)
	Dairy manure	350/450/500	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH, Cl), Pb <sub>9</sub> (PO <sub>4</sub> ) <sub>6</sub> , Pb <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub> , PbCO <sub>3</sub>	Cao et al. (2009), Xu et al (2013)
	Digested sugar beet/Sugarcane bagasse	600	Pb <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	Inyang et al. (2012)
	Peanut shell/Medicine residues	300/350/400	Pb <sub>2</sub> (SO <sub>4</sub> )O, Pb <sub>4</sub> (CO <sub>3</sub> ) <sub>2</sub> (SO <sub>4</sub> )(OH) <sub>2</sub>	Wang et al. (2015)
	Sludge	550	PbO·P <sub>2</sub> O <sub>5</sub> ·SiO <sub>2</sub>	Lu et al. (2012)
	Water hyacinth	450	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH, Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	Yin et al. (2016)
	Dairy manure	350	Cd <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Xu et al. (2013)
Cd	Nut shield/plum stone/Grape stalk	600	CdCO <sub>3</sub>	Trakal et al. (2016)
	Water hyacinth	450	CdCO <sub>3</sub> , Cd <sub>3</sub> P <sub>2</sub> , Cd <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , K <sub>4</sub> CdCl <sub>6</sub>	Zhang et al. (2015a)
	Wheat straw/S. hermaphrodita	700	CdO	Bogusz et al. (2015)
Cu	Pecan shell	700	Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH <sub>2</sub> ), CuO	Ippolito et al. (2012b)
	Rice husk	300-400	Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Arán et al. (2016)
	Swine manure	400/700	CuSiO <sub>3</sub> , K-Cu-PO <sub>4</sub> , Ca-Cu-PO <sub>4</sub>	Meng et al. (2014)
	Wheat straw/S. hermaphrodita	700	Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH <sub>2</sub> ), Cu <sub>2</sub> O	Bogusz et al. (2015)
Zn	Meat and bonemeal	-	ZnPO <sub>4</sub>	Betts et al. (2013)
	Miscanthus	860	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Wagner et al. (2015)
	Wheat straw/S. hermaphrodita	700	ZnO	Bogusz et al. (2015)
Hg	Wood/Manure	300/600	HgCl <sub>2</sub> , Hg-O, Hg-S	Liu et al. (2016)
Cr	Sewage sludge	900	Cr(OH) <sub>3</sub>	Chen et al. (2015b)
As	Water hyacinth	450	Ca <sub>5</sub> (AsO <sub>4</sub> ) <sub>3</sub> OH, Ca <sub>4</sub> (OH) <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	Yin et al. (2016)

**Table 3**

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 <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup> , SiO <sub>4</sub> <sup>4-</sup> , etc.
	Cation exchange	Minerals containing K, Na, Ca, Mg, etc.
	Electrostatic attraction	SiO <sub>2</sub> , etc.
Organic pollutant removal (PAH, etc.)	Cation-π interactions	Minerals containing Fe, Mg, Si, K, Ca, etc
	Surface complexation	Minerals containing OH, etc.
PO <sub>4</sub> <sup>3-</sup> removal	Precipitation	Mineral containing Ca, etc.
	Electrostatic attraction	Mg oxide, etc.
	Surface inner-sphere complexation	Fe oxide, etc.
NH <sub>4</sub> <sup>+</sup> removal	Cation exchange	Minerals containing K, Na, Ca, Mg, etc.
Acidic gases removal (H <sub>2</sub> S, SO <sub>2</sub> , CO <sub>2</sub> , 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 <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>
	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 <sub>3</sub> , and CaCO <sub>3</sub> , etc.
	Improving water-holding capacity	Minerals containing electron-deficient metals, such as Al
	Retention of P	Fe and Al oxides



**Fig. 1**

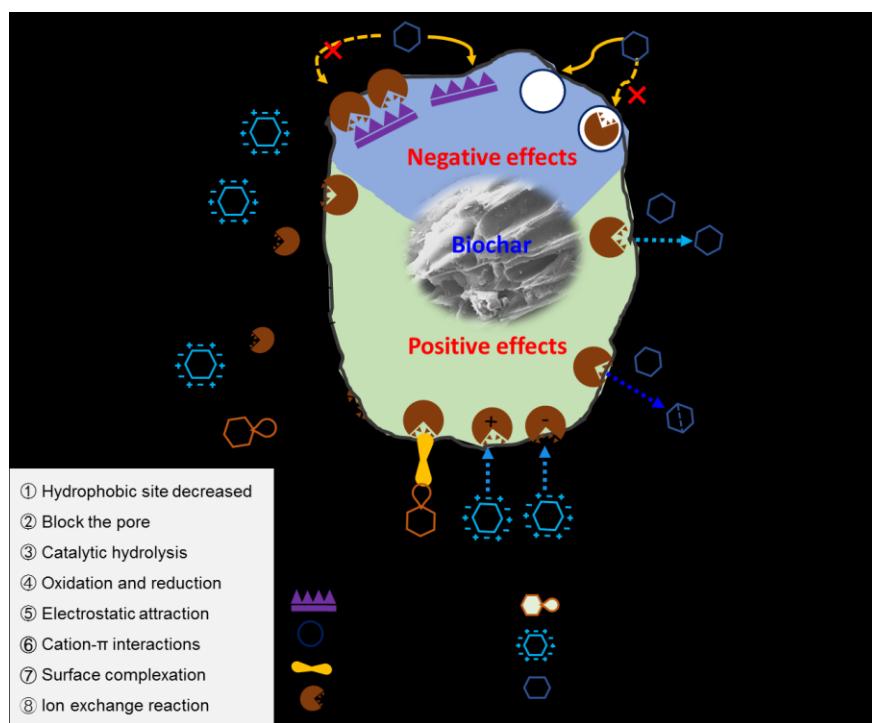
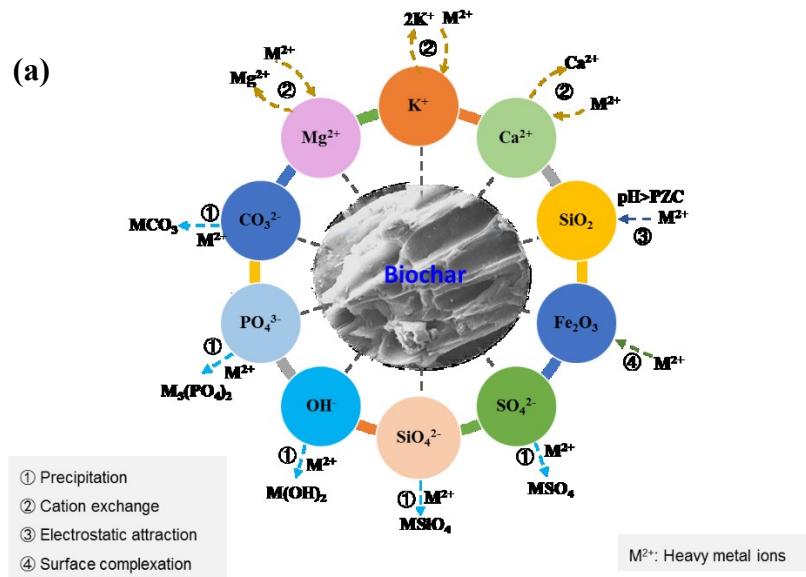


Fig. 2

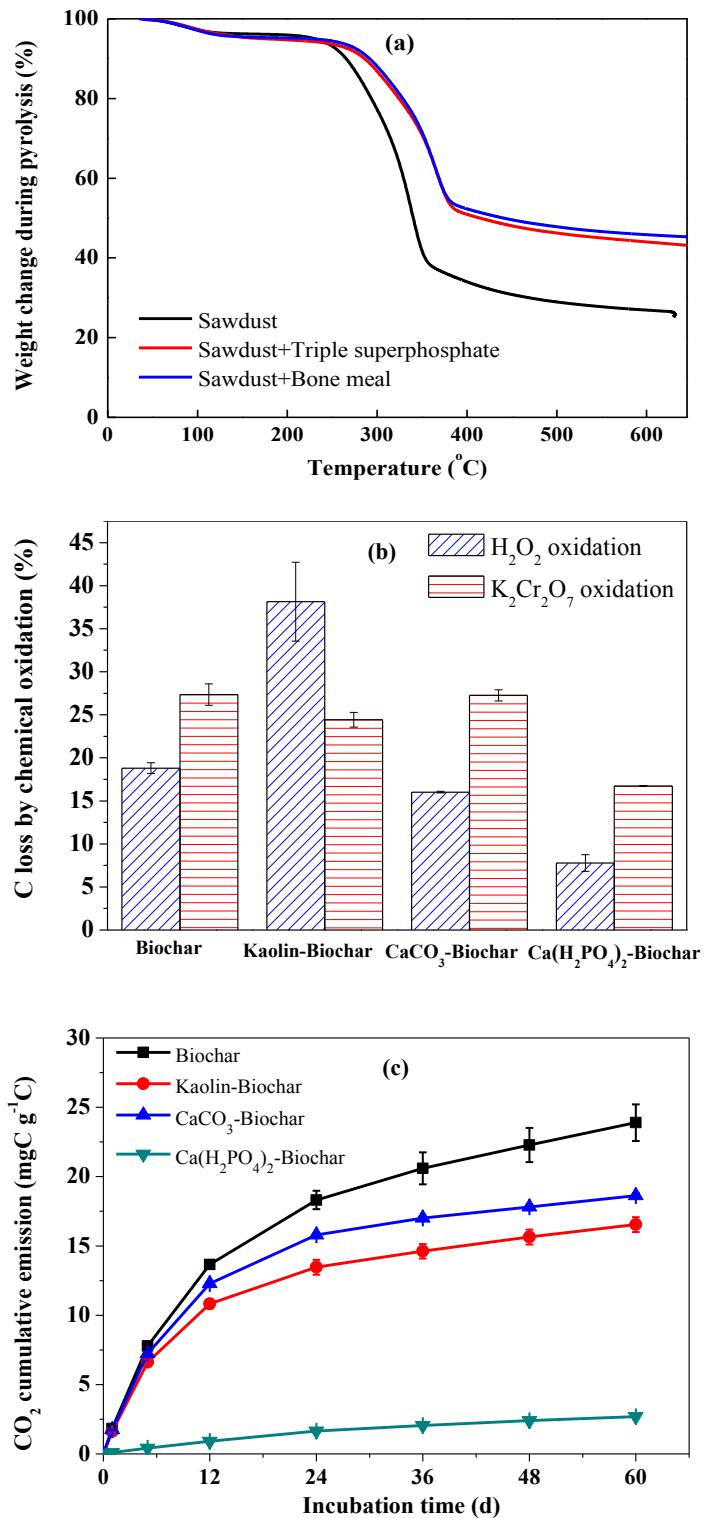


Fig. 3