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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.

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

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 CO₂ (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

testing of more feedstock for biochar applications, it has become apparent that mineral fractions could influence the properties of biochar and thus directly or indirectly influence its applications (Buss et al., 2016b; Gunes et al., 2015; Yuan et al., 2011). For example, mineral components, such as Ca, Mg, K, and P, may allow biochar to act as a direct source of mineral nutrients, promoting plant growth (Amini et al., 2015); anions such as OH^- , CO_3^{2-} , PO_4^{3-} and SO_4^{2-} , released from biochar minerals, play an important role in the removal of heavy metals by the formation of metal precipitates (Inyang et al., 2015). On the other hand, high contents of certain minerals, especially toxic heavy metals, in the biochar could raise health concerns (Buss et al., 2016a) and could also limit the sorption of organic compounds if these biochars are not de-ashed prior to their use in applications requiring the sorption of organic compounds (Sun et al., 2013; Zhang et al., 2013a).

A variety of aspects of biochar, including its production, properties, and applications, have been reviewed extensively (Xie et al., 2015; Inyang et al., 2015). However, there is no review dealing with the role of the mineral fraction of biochar in its properties and applications. This paper aims to present a critical review of the indispensable role of biochar inherent mineral fractions in controlling its properties and applications, especially environmental applications. Specifically, the effect of the mineral fraction on the following aspects will be systematically reviewed: (1) physicochemical properties of biochar, (2) contaminant sorption by biochar, (3) carbon retention and stability of biochar, (4) nutrient bioavailability of biochar, and (5) emerging applications of biochar as a precursor for fuel cells, supercapacitors, and photoactive components.

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 (KH_2PO_4), chlorocalcite (KCaCl_3), kalcinite (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 (KCl). The most common
93 minerals present in biochars include sylvite (KCl), quartz (SiO_2), amorphous silica,
94 calcite (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

discrete mineral phases or are associated with the surface functional groups of biochars (Wang et al., 2015).

The mineral content of biochar generally increases with increasing pyrolysis temperature (Table 1). For example, Song et al (2012) reported that the content of K, Ca, Mg, and P in biochars derived from poultry manure increased by 32.0%, 30.9%, 30.1%, and 34.4%, respectively, when pyrolysis temperature increased from 300 °C to 600 °C. This is because as the pyrolysis temperature is increased, the organic constituents of biomass, including cellulose, hemicelluloses, and lignin are, to a large extent, converted and released in the form of volatiles and gases while the much less volatile mineral compounds, such as Mg, Ca and P, remain and are thus concentrated in biochar (Zhang & Wang, 2016). In addition to the enrichment caused by the increase of pyrolysis temperature, the minerals in biochars may also become more crystallized and less soluble, especially above 500 °C (Cao & Harris, 2010; Yuan et al., 2011). Therefore, the solubility of mineral components reduces with increasing temperature, as shown in Table 1. Wang et al. (2015) reported that the soluble $\text{PO}_4^{3-}\text{-P}$ in peanut-shell-derived biochar decreased from 430 to 70 mg kg^{-1} when the pyrolytic temperature increased from 300 °C to 600 °C, due to the formation of less soluble crystalline 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. Additionally, new mineral species may also be formed as the pyrolysis temperature is increased. Qian et al. (2016) showed that new minerals, such as magnesia calcite (MgCO_3), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), appeared in rice-straw biochar when the production temperature was increased from 100 °C to 500 °C.

In addition to the above-mentioned “good” mineral elements, biochar may contain some “bad” mineral elements, i.e., potentially toxic elements. The content and availability of these elements is also significantly affected by the feedstock and

pyrolysis conditions of biochar. Buss et al. (2016a) and Khanmohammadi et al. (2015) found that the percentage of available, potentially toxic elements, such as Cr, Ni, Cu and Zn, increased with increasing pyrolysis temperature, particularly when the temperature was increased from 600 °C to 750 °C.

Both feedstock and production conditions are important for determining the mineral constituents of biochar, but the content of key minerals in biochar shows a linear dependence on the levels within the initial feedstock (Alexis et al., 2007). This suggests that the selection of biochar for soil amendment, aimed at improving soil fertility by the addition of nutrients, should preferentially focus on feedstock selection rather than the production temperature, although the pyrolysis temperature can affect the availability of nutrients in biochar (Zhao et al., 2013).

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

Mineral elements, such as K, Na, Si, Mg, and Ca, can be involved in the carbonization processes of biomass, thus influencing the pyrolysis reactions and products (Chen et al., 2008b; Yang et al., 2006). Chen et al. (2008b) studied the catalytic effects of inorganic additives on the pyrolysis of pine wood sawdust, pointing out that Na additives could greatly increase the yield of solid products (biochar) and decreased yield of gaseous products. Yang et al. (2006) showed that K₂CO₃ inhibited the pyrolysis of hemicellulose while enhanced the pyrolysis of cellulose by shifting the pyrolysis to a lower temperature. This obvious catalytic effect of K₂CO₃ might be attributed to certain fundamental changes in terms of chemical structure of hemicellulose or decomposition steps of cellulose in the course of pyrolysis. As a result, mineral-induced pyrolysis reactions of biomass may affect the physical and chemical properties, such as the pH, electric conductivity (EC), cation exchange capacity (CEC), specific surface area

(SSA), structure, and morphology, of biochar (Zhang & Wang, 2016). This section focuses on the relationship between the biochar mineral (ash) and its key properties.

The International Biochar Initiative (IBI) has graded biochar into three classes, based on the carbon content: Class 1 biochar contains 60% carbon or more; Class 2 biochar contains 30%-60% carbon; and Class 3 biochar contains 10%-30% carbon ([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 rather than the total C. Since the content of organic C in biochar is much larger than inorganic C, total C is used to represent organic C for the classification in this study.

Figure 1a and Table S1 summarize the negative relationship between the carbon content and mineral content ($R^2=0.76$), showing that most Class 1 biochars contain less than 20% minerals; Class 2 biochars contain 20%-60% minerals; and the mineral content of Class 3 biochars is higher than 60%. Therefore, in order to discuss the effect of minerals on the properties of biochar, we also categorize biochar into three classes, based on the mineral content. These include: Class 1 biochar (below 20% minerals), Class 2 biochar (between 20% and 60% minerals), and Class 3 biochar (containing 60% minerals or more). Note that this classification may not map exactly with the IBI classification, e.g., some biochars may have low ash content as well as a low carbon content due to high H, N, and O contents. However, the carbon content of most biochars is negatively related to the mineral content ($R^2=0.76$), based on the 278 biochar samples summarized in this papers (Table S1). Therefore, this classification is acceptable for the present review.

3.1. C content

For Class 1 biochars, mostly derived from plant residues, no strong correlation between mineral content and carbon content is observed (Table 1, Table S1, and Fig.

1a). This is likely due to the low mineral content, because of which its effects can be masked by those of other constituents, e.g., H, O, and N. However, as the mineral content increases (Class 2 and Class 3 biochars), a strong negative correlation between carbon content and ash content can be observed (Fig. 1a). Singh et al. (2010) found that the C values in low-ash biochar increased with the increase in pyrolysis temperature, whereas the reverse trend was found for high-ash biochar. This discrepancy was due to the dramatically different contents of ash, which was not volatilized and enriched with increasing temperature (Zhang & Wang, 2016). Minerals not only influence the carbon content of biochar but also affect the distribution of carbon in the surface and bulk. Sun et al. (2013) found that after de-ashing the surface C content of manure-derived biochars decreased while the total C increased. However, the authors also noted that this was not the case for biochar derived from plant residues, in which inherent minerals had no discernible effect on the spatial distribution of carbon (Sun et al., 2013). Therefore, the nature and distribution of minerals in biomass play important roles in the content and distribution of carbon in the resulting biochar.

3.2. *pH*

For biochars of all three classes, most of them were alkaline ($\text{pH} > 7.0$) (Fig. 1b). Yuan et al. (2011) and Hass et al. (2012) showed that alkali metals (Na, K) or alkaline earth metals (Ca, Mg) in the form of carbonates are the main alkaline substances responsible for the high pH of biochar derived from crop residues and chicken manure. In their work, a positive correlation between the alkalinity of biochar and its ash content was observed. However, Fig. 1b shows a weak correlation between ash content and pH. Xu et al. (2016b) found that sludge biochar had a much higher mineral content than wheat-straw biochar, but its pH was lower. This can be explained by the abundance of

Fe in sludge biochar, since Fe may cause hydrolysis, producing H^+ in the solution. Therefore, the mineral composition, rather than content, has a greater effect on the pH of biochar. Functional groups such as $-COO^-$ ($-COOH$) and $-O^-$ ($-OH$) also contributed to the alkalinity of the biochars, especially for those generated at the lower temperature (Yuan et al., 2011). The pH of biochar samples increased with increasing pyrolysis temperature. This is because a higher pyrolysis temperature can remove acidic functional groups (e.g. $-COOH$ and $-OH$) and promote the separation of minerals such as KOH, NaOH, $MgCO_3$, and $CaCO_3$ from the solid carbon matrix, resulting in elevated pH values (Meng et al., 2013; Mohan et al., 2014). Furthermore, the existence of these alkaline minerals enhanced the buffering capacity of biochar (Xu & Chen, 2014).

3.3. Porosity

Class 1 biochars with a low mineral content show a higher specific surface area (SA, up to $650\text{ m}^2\text{ g}^{-1}$) and pore volume (PV, up to $1.40\text{ cm}^3\text{ g}^{-1}$) than Class 2 and 3 biochars (SA, below $200\text{ m}^2\text{ g}^{-1}$; PV, below $0.45\text{ cm}^3\text{ g}^{-1}$), indicating that a high ash content could reduce the surface area and pore volume of biochar (Fig. 1c). It was reported that ash in biochar might fill or block access to micropores (Agrafioti et al., 2013). Sun et al. (2011) found that animal-waste biochars had a lower surface area than plant-based biochars produced at the same pyrolysis temperature and residence time due to the higher mineral contents of most animal-waste biochars. The surface area and pore volume of carbonaceous materials can be greatly improved by base- or acid-treatments since the base-leaching procedure can effectively remove ash (mostly silica) and the acid-washing procedure can act as a cleaning process to remove metallic impurities (Liou & Wu, 2009). Therefore, high-surface-area biochar can be produced from high-ash biochar by de-ashing of the char.

3.4. Surface chemistry

Minerals can also influence the surface electrochemistry and ion-exchange properties of biochar. Buss et al. (2016b) found that the electric conductivity (EC) of biochars (used for approximation of salinity) was well-correlated with the ash content ($R^2 = 0.75$). Zhao et al. (2015) found that the point of zero charge (PZC) of plant-based biochars was lower than that of solid-waste-based ones, probably due to the low content of minerals. Minerals such as SiO_2 were highly negatively charged, even at lower pH values due to their low isoelectric point (~ 2.0) (Waseem et al., 2010). The cation exchange capacity (CEC) and anion exchange capacity (AEC) also showed strong positive correlation with soluble cations and anions, respectively (Zhao et al., 2015).

As discussed above, minerals can affect the physicochemical properties of biochar. Thus, engineered biochar was designed by impregnation of minerals (Yao et al., 2013; Zhang et al., 2012) or by using a demineralization treatment to impart or improve the desirable properties of biochar (Liu et al., 2015).

4. Role of minerals in the sorption of contaminants

The removal of organic and inorganic contaminants from water and soil has been extensively reviewed (Inyang et al., 2015; Mohan et al., 2014; Tan et al., 2015). This section focuses on the role of the mineral components of biochar in the sorption of contaminants, including heavy metals, organic contaminants, N and P, acidic gases, etc.

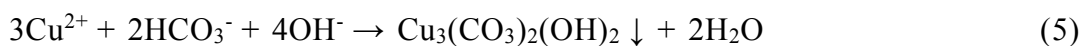
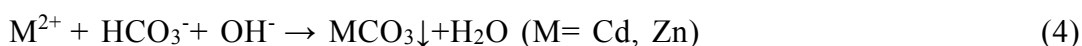
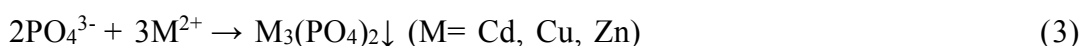
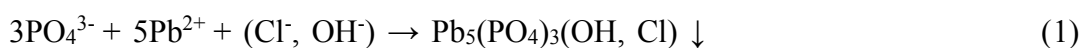
4.1 Heavy metals

An increasing number of studies have shown that both carbon and mineral fractions of biochar can contribute to immobilization of heavy metals (Qian & Chen, 2013; Qian et al., 2016). For biochars with a low mineral content, including some crop

residue biochars, the sorption of heavy metals occurs mainly through the formation of surface complexes between heavy metals and organic O-containing functional groups (e.g., -COOH, alcoholic -OH or phenolic -OH) on biochar (Tong et al., 2011). However, for biochars rich in minerals, such as manure biochar and sludge biochar, interactions between heavy metals and mineral components may be the dominant factor in sorption (Cao et al., 2009; Lu et al., 2012; Zhang et al., 2013b). Minerals could be responsible for up to 90% of metal removal by biochars (Wang et al., 2015; Xu et al., 2014). Four different possible mechanisms of heavy metal removal by biochar are summarized here and schematically shown in Fig. 2a: (i) electrostatic attraction between cationic (or anionic) metals and negatively (or positively) charged minerals; (ii) cation exchange between metal ions and mineral ions (e.g., K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) associated with surface functional groups of biochar or present in the biochar; (iii) co-precipitation and inner-sphere complexation of metals with mineral oxides of the biochar; and (iv) precipitation of heavy metals with anions released from minerals (e.g., OH^- , CO_3^{2-} , PO_4^{3-} , SO_4^{2-} and SiO_4^{4-}).

Various precipitates can be formed during the sorption of heavy metals by different mineral-containing biochars (Table 2). Lead carbonates (e.g., $PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$) and lead phosphates (e.g., $Pb_5(PO_4)_3(OH, Cl)$ and $Pb_9(PO_4)_6$) are the most common precipitates formed in the sorption of Pb by biochars (Inyang et al., 2012; Yin et al., 2016) (Table 2). The possible precipitation reactions have been proposed and are shown below (Cao et al., 2009; Xu et al., 2013) (Reactions 1-2). Apart from these two types of precipitates, new mineral precipitates, e.g., $Pb_2(SO_4)O$, $Pb_4(CO_3)_2(SO_4)(OH)_2$ (Wang et al., 2015), and $PbO \cdot P_2O_5 \cdot SiO_2$ (Lu et al., 2012), were also found during the sorption of Pb^{2+} by biochars. Like Pb, carbonate and phosphate precipitates were found in the sorption of Cd (Trakal et al., 2016), Cu (Arán et al., 2016;

Ippolito et al., 2012b), and Zn (Betts et al., 2013; Wagner et al., 2015) by biochars (Table 2). Reactions 3-5 are the possible precipitation reactions that have been proposed (Xu et al., 2013). Additionally, oxide precipitates (e.g., CdO and ZnO) were also observed by Bogusz et al. (2015). Meng et al. (2014) reported that silicate particles within the biochars served as adsorption sites for Cu(II), and CuSiO₃ was the final product. Co-precipitation of silicate particles with Al (as KAlSi₃O₈) was also observed by Qian and Chen (2013). The sorption of Hg can occur by its precipitation as HgCl₂, HgO, or HgS on alkaline biochar surfaces containing high chloride or sulfur contents (Liu et al., 2016).



The precipitation of oxyanionic metals, such as As and Cr, with biochar minerals has rarely been reported and is greatly influenced by their valence state (Chen et al., 2015; Yin et al., 2016). For example, Cr(III) is much easier to stabilize than Cr(VI) and can precipitate as Cr(OH)₃ during sorption (Chen et al., 2015). The sorption of Cr(VI) may be enhanced by biochar minerals such as alkaline metals (Shen et al., 2012), but there is limited evidence of the formation of precipitates between them. This is because Cr(VI) is removed by reduction to Cr(III) by the functional groups of biochar (Dong et al., 2011). It was reported that Ca₅(AsO₄)₃OH and Ca₄(OH)₂(AsO₄)₂(H₂O)₄ were found in the sorption of As(V) by biochar derived from water hyacinth (Yin et al., 2016). Note that both soluble and insoluble minerals of biochar play important roles in the sorption of heavy metals, but the adsorption affinity of water-soluble fractions is much higher

than that of water-insoluble minerals (Xu & Chen, 2014). The solubility of minerals could also influence the sorption kinetics of heavy metals. Since metal removal was mainly attributed to the precipitation of heavy metals by anions (e.g., PO_4^{3-} and CO_3^{2-}) released from minerals in biochars, the sorption rate was controlled by the dissolution of the minerals (Wang et al., 2015). In low-temperature biochar, the minerals were amorphous, more soluble, and easier to release for subsequent precipitation with heavy metals (Zheng et al., 2013). On the other hand, in high-temperature biochar, the minerals were more crystallized, less soluble, and more difficult to release (Cao & Harris, 2010). Uchimiya et al. (2012) and Cao et al. (2009) reported that the dairy manure biochar produced at higher temperatures ($>500\text{ }^\circ\text{C}$) had a lower content of soluble P due to the association of stable P-Ca-Mg, which was not favorable for the release of P and its subsequent precipitation with Pb. Therefore, the sorption kinetics of biochar produced at low temperatures is faster than that of biochar produced at high temperatures.

Cation exchange between biochar mineral elements and heavy metals is also an important mechanism for metal removal. Uchimiya et al. (2010) suggested that as the degree of biochar carbonization and loading of chars increases, heavy metal immobilization by cation exchange becomes increasingly outweighed by other controlling factors, such as the coordination by π electrons ($\text{C}=\text{C}$) of carbon and precipitation. The solubility of minerals in the biochar also influences the cation exchange ability. Therefore, biochar produced at a low pyrolysis temperature is favorable for immobilizing heavy metals due to the large release of available mineral components, such as K and Ca, as well as a low degree of carbonization (Uchimiya et al., 2012).

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

electrostatic adsorption of heavy metals. Biochar surface charges depend not only on surface functional groups but also on mineral components (Zhao et al., 2015). Biochar rich in SiO₂ is negatively charged, even at lower pH values (pH <3.0), due to its low isoelectric point (~2.0). Therefore, adsorption of heavy metal ions still occurs, even in low pH ranges (1.5~3.0), by electrostatic adsorption on the SiO₂ components (Xu & Chen, 2014).

Since minerals play an important role in the sorption of heavy metals, the sorption efficiency is dramatically reduced after biochar is demineralized or de-ashed. Thus, attempts have been made to increase the sorption capacity of biochar by adding minerals to it. For example, Mn-oxide-modified and birnessite-modified biochars were prepared for the purpose of improving the sorption abilities for As³⁺, Pb²⁺, and Cu²⁺ (Song et al., 2014). However, not all minerals are equally effective or favorable for the removal of heavy metals by biochars, and mineral-rich biochars should be used with caution.

4.2. Organic contaminants

Compared to heavy metals, much less work has been done to study the impact of minerals on the sorption of organic contaminants by biochar. However, the presence of minerals has been found to have at least an indirect influence on the sorption of organic contaminants by biochar (Smernik, 2009). For example, minerals may influence the spatial arrangement of organic matter within biochars or the formation of aromatic structures during pyrolysis, and thus affect the sorption behavior of biochar (Smernik, 2009; Sun et al., 2013). Additionally, the significantly different sorption performances of biochar before and after mineral removal indicate that minerals could directly influence the sorption of organic contaminants by biochar (Sun et al., 2013). Since the

specific type of contaminant can impact the sorption properties of biochar, different minerals might exhibit different effects towards these contaminants.

The ability of biochar to sorb hydrophobic organic contaminants (HOCs) is closely related to the surface and bulk properties of its carbon fraction, including the graphene-like carbon fraction and the non-crystalline amorphous carbon fraction in biochar. Pore-filling, partitioning, hydrophobicity, aromatic- π interactions, etc. have been proposed as key sorption mechanisms (Zhang et al., 2013a). Therefore, to date, most sorption studies for HOCs have used carbon-rich and low-mineral biochars produced from relatively pure plant residues. In addition, many studies have proven that the presence of minerals is not favorable for the sorption of HOCs. Thus, high-mineral biochars are de-ashed or de-mineralized using acid/alkaline and/or water rinses prior to their use for HOC-sorption. For example, Sun et al. (2013) reported that the organic carbon (OC)-normalized distribution coefficients (K_{oc}) of phenanthrene by biochars generally increased after de-ashing, likely due to the enhancement of favorable and hydrophobic sorption sites by the removal of minerals. Zhang et al. (2013a) stated that the adsorption of carbaryl and atrazine increased greatly after biochar was de-ashed, as the removal of mineral compounds unblocked previously inaccessible organic adsorption sites in the original biochars. De-mineralization and de-ashing treatments can greatly influence the composition and surface characteristics of the biochar, and thus significantly improve the adsorption properties of biochar (Tan et al., 2015).

On the other hand, the hydrolysis and reduction of hydrophobic organic contaminants could be enhanced with the presence of minerals. For example, Zhang et al (2013a) showed that hydrolysis of carbaryl and atrazine was enhanced due to the catalytic effects of elevated pH, solid mineral surface, and the released dissolved metal 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- π 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

on the mineral surface and carboxyl groups on the organic contaminants; and (4) ion exchange reactions. Ji et al. (2011) proved that the mineral fraction played an important role in the tetracycline adsorption by crop residue-derived biochar, due to strong surface complexation of tetracycline with the mineral components via surface complexation (such as H-bonding) and/or ion exchange reactions.

As illustrated in Fig. 2b, different minerals have different impacts on the sorption of various types of organic contaminants, such as polar and non-polar, and ionic and non-ionic organic contaminants, by biochar. Therefore, biochars with the appropriate mineral contents and species should be chosen for the removal of specific contaminants. Research on interactions between biochar mineral matter and organic contaminants is needed to provide such reliable prescriptions.

4.3. *N and P*

In addition to being a potentially important sorbent for organic pollutants and heavy metals, biochar can also act as a potential sorbent for recovering nutrients (NH_4^+ and PO_4^{3-}) (Sarkhot et al., 2013). Generally, the surfaces of most carbon-rich and low-mineral biochars are negatively charged and have little or no ability to remove anions, particularly PO_4^{3-} (Jung et al., 2015; Yao et al., 2011). For example, Jung et al. (2015) discovered that biochars derived from soybean stover, bamboo wood, and maize residue showed no sorption capacity for PO_4^{3-} removal and even released inherent PO_4^{3-} into the solution. However, Sarkhot et al. (2013) found that biochar produced from mixed hardwood could effectively sorb PO_4^{3-} via exchange with its surface hydroxyl groups.

Compared to low-mineral biochar, biochars with high mineral content, mainly Ca and Mg, usually show a higher capability to sorb phosphate. This sorption ability is 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 PO_4^{3-} through precipitation. Streubel et al. (2012) reported that co-precipitation as Ca-phosphates was the main mechanism for 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), 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 MgO and $\text{Mg}(\text{OH})_2$ particles within the biochar matrix. The points of zero charge of $\text{Mg}(\text{OH})_2$ and 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 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 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 NH_4^+ adsorption. On the other hand, Sarkhot et al. (2013) observed a relatively high degree of correlation between the amount of sorbed NH_4^+ and the amount of cations released by biochar, especially Ca^{2+} ($R^2 = 0.65$), indicating that cation exchange between Ca^{2+} in the biochar

and NH_4^+ was the likely mechanism for NH_4^+ adsorption.

In conclusion, minerals, especially Ca and Mg, play an important role in the sorption of NH_4^+ and PO_4^{3-} by biochar via precipitation, cation exchange, and electrostatic interactions. Biochar with high contents of Ca and Mg could act as a sorbent for nutrients (NH_4^+ and PO_4^{3-}). The nutrient-enriched biochar obtained after sorption can be used as a slow-release fertilizer in horticulture and agriculture.

4.4. Acidic gas

Biochars with high contents of alkali and alkaline earth metals (K, Ca and Mg, etc.) are often highly alkaline, which favors dissolution of acidic gases, such as SO_2 , H_2S , and CO_2 , and consequently enhances the removal of these acidic gases. Shang et al. (2013) reported that biochars produced from a series of agricultural/forestry residues, such as rice hull, camphor, bamboo, and rice hull, were effective for the sorption of H_2S . They attributed the sorption ability to the high local pH within the pore systems of these biochars. Some mineral oxides, such as zinc and iron oxides, present in biochars might be effective oxidants for the removal of H_2S (Azargohar & Dalai, 2011). Xu et al. (2016b) stated that the carbon fraction of biochar could catalyze the conversion of H_2S to elemental S^0 and S(VI) (Reactions 6-9), while the minerals could further react with the produced SO_4^{2-} , forming CaSO_4 precipitate (Reaction 10) in the sewage sludge biochar and $(\text{K}, \text{Na})_2\text{SO}_4$ in the pig manure biochar. In addition to H_2S , SO_2 could also be effectively removed by biochar derived from dairy manure, sludge, and rice husk, as reported by Xu et al. (2016b). In their work, CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$ in dairy-manure biochar induced the conversion of the sorbed SO_2 into $\text{K}_2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; in sludge biochar, the sorbed SO_2 was converted to $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$. $\text{K}_3\text{H}(\text{SO}_4)_2$ might exist in the exhausted

samples of rice-husk biochar. The chemical transformation of SO₂, induced by inherent mineral components, accounts for 44.6%-85.5% of the SO₂ sorption by biochar (Xu et al., 2016b).



Mineral components, such as Mg, Ca, Fe, K, etc., in biochar may convert sorbed CO₂ to bicarbonate/carbonate (Xu et al., 2016b). In order to determine the role of mineral components in the sorption of CO₂ by biochar, Xu et al (2016b) separated the minerals from biochars and used them for CO₂ sorption. XRD analysis of minerals after CO₂ sorption showed that the sorbed CO₂ was transformed to K₂Ca(CO₃)₂ and CaMg(CO₃)₂ by pig-manure biochar minerals (Fig. S1a), and to CaMg(CO₃)₂ by wheat-straw biochar minerals (Fig. S1b).

Since minerals in biochar could enhance the capture of acidic gases, impregnation of minerals, such as magnesium hydroxide and iron oxide, into biochar has been used by some authors to improve the performance of original biochars (Creamer et al., 2016). However, the application of biochar for the sorption of acidic gases is still in its infancy and needs further investigation.

5. Effect of minerals on carbon loss and carbon stability

The “biochar” concept was initially developed for dealing with the challenges of climate change caused by the greenhouse effect. It has been proposed that the relatively 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 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.

6. Effect of minerals on nutrient value of biochar

Many studies have reported that biochar can be used for soil amendment to improve soil quality and increase crop production. In this regard, an obviously positive

attribute of biochar is its nutrient value, supplied either directly by providing nutrients to plants or indirectly by improving the soil quality. Since the details on soil are out of scope of Bioresource Technology, this section is only shown in Supporting Information.

7. Effect of minerals on other applications of biochar

In addition to the fields discussed in the previous sections, minerals may also play an important role in other applications, including fuel cell precursors, supercapacitors, or as photoactive components. It has been reported that sludge biochar has a very high catalytic activity for the Oxygen Reduction Reaction (ORR) in a microbial fuel cell. Here, a high surface area and the higher N and Fe contents of biochar might have jointly contributed to the high catalytic activity (Yuan et al., 2013). Ahn et al. (2013) investigated the utilization of wood biochar in the direct carbon fuel cell (DCFC) system and found that the performance of this higher ash biochar could reach 60–70% of that of coal. However, the role of minerals in the DCFC system was not fully elucidated, and the author attributed the potential of biomass char as a DCFC fuel to its porous characteristics and the functional groups on the char surface (Ahn et al., 2013). Another area where biochar has gained a foothold is in the production of electrodes for supercapacitors, which are essential electric devices for energy storage (Kai et al., 2015). Although the minerals might not favor the capacitive performance of biochar capacitor following the electric double-layer mechanism (Abioye & Ani, 2015), the capacitor containing metal hydroxides, transition metal oxides could have a great pseudo-capacitive ability (Wang et al., 2017). Wang et al (2017) found that Ni-rich biochar could be converted into supercapacitors with both pseudo-capacitive and electric double-layer properties. They attributed the increase of capacitance in the Ni-rich biochar supercapacitor to the existence of NiO and NiOOH (Wang et al., 2017). In

addition to applications in fuel cells and supercapacitors, Fu et al. (2015) noted that dissolved black carbon released from biochar can be one of the more photoactive components in the dissolved organic matter (DOM) pool, and silica minerals in dissolved biochar could mediate electron transfer reactions that are responsible for the generation of superoxide.

From the above discussion, it is clear that biochar has various conventional and emerging applications, in which inherent minerals play a variety of roles. A thorough understanding of the role of biochar-bound minerals in different applications will allow the design or selection of the most suitable biochar, with minerals appropriate for specific applications. Table 3 summarizes the preferred minerals addition to the designed biochar for specific applications. Production and application of the designed biochar with mineral incorporation has a great research prospect which will be our future study.

8. Conclusions

The biochar-inherent minerals have the potential to influence its physicochemical properties and its performance in different applications. However, the understanding of the role of mineral components in biochar is fairly limited, and greater efforts must be made across many areas, such as (1) the bioavailability of toxic metals contained in certain types of biochar; (2) the role of biochar-inherent minerals in carbon sequestration and other emerging applications, e.g., as a precursor of catalysts and photoactive components; and (3) design of biochar for specific applications by incorporating appropriate minerals into feedstock or biochar.

Supporting Information

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

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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 CO₂ 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	Corn cob	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 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 ₂ O ₅ ·SiO ₂	Lu et al. (2012)
	Water hyacinth	450	Pb ₅ (PO ₄) ₃ OH, Pb ₅ (PO ₄) ₃ Cl	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 ₃ P ₂ , Cd ₃ (PO ₄) ₂ , K ₄ CdCl 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 ₂ O	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 ₂ O	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) ₃ OH, Ca ₄ (OH) ₂ (AsO ₄) ₂ (H ₂ O) ₄	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 Cation exchange Electrostatic attraction	Minerals containing OH^- , CO_3^{2-} , PO_4^{3-} , SO_4^{2-} , SiO_4^{4-} , etc. Minerals containing K, Na, Ca, Mg, etc. SiO_2 , etc.
Organic pollutant removal (PAH, etc.)	Cation- π interactions Surface complexation	Minerals containing Fe, Mg, Si, K, Ca, etc Minerals containing OH, etc.
PO_4^{3-} removal	Precipitation Electrostatic attraction Surface inner-sphere complexation	Mineral containing Ca, etc. Mg oxide, etc. 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 Formation of Si-encapsulated carbon	Minerals containing P, e.g. $\text{Ca}(\text{H}_2\text{PO}_4)_2$ Minerals containing Si
Soil amendment	Direct nutrient release Increasing CEC Liming effect Improving water-holding capacity Retention of P	Plant macro- and micro-nutrients Minerals containing basic cations, such as K, Na, Ca, Mg KOH , NaOH , MgCO_3 , and CaCO_3 , etc. Minerals containing electron-deficient metals, such as Al Fe and Al oxides

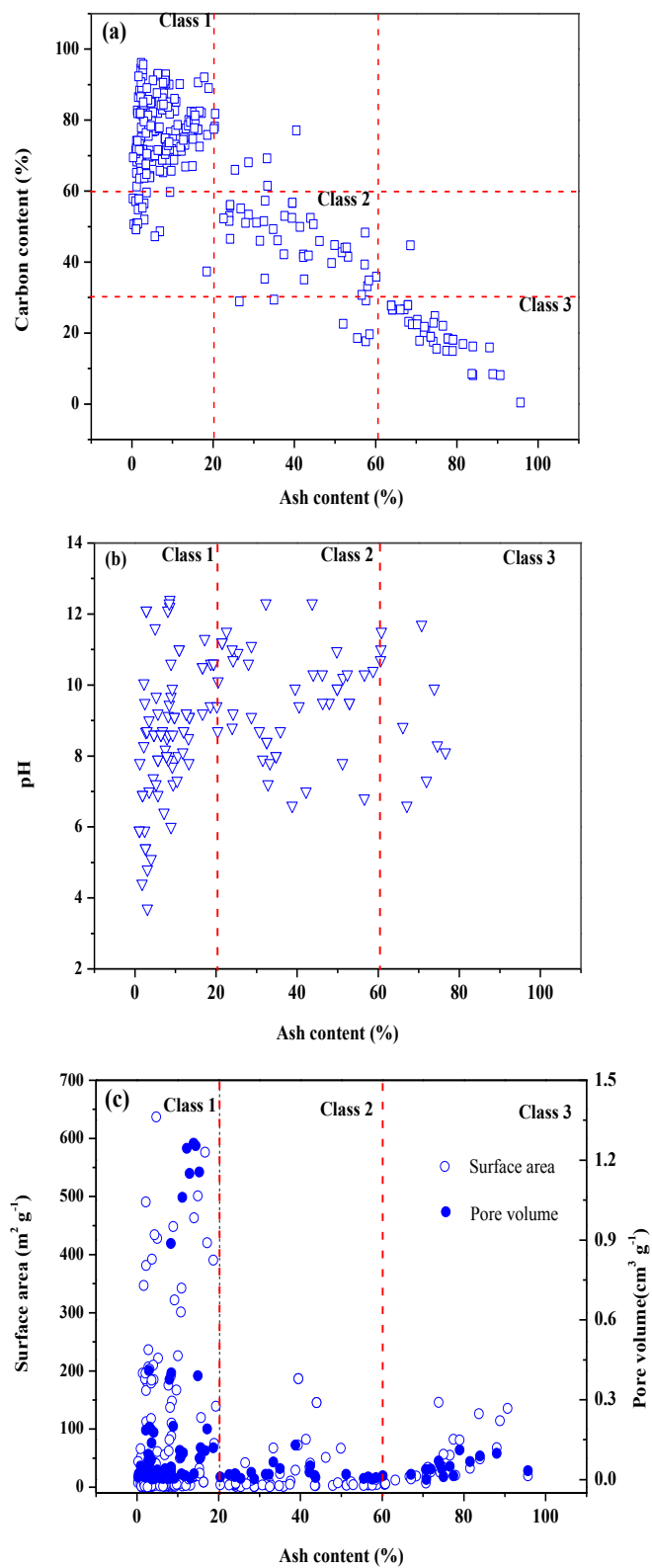


Fig. 1

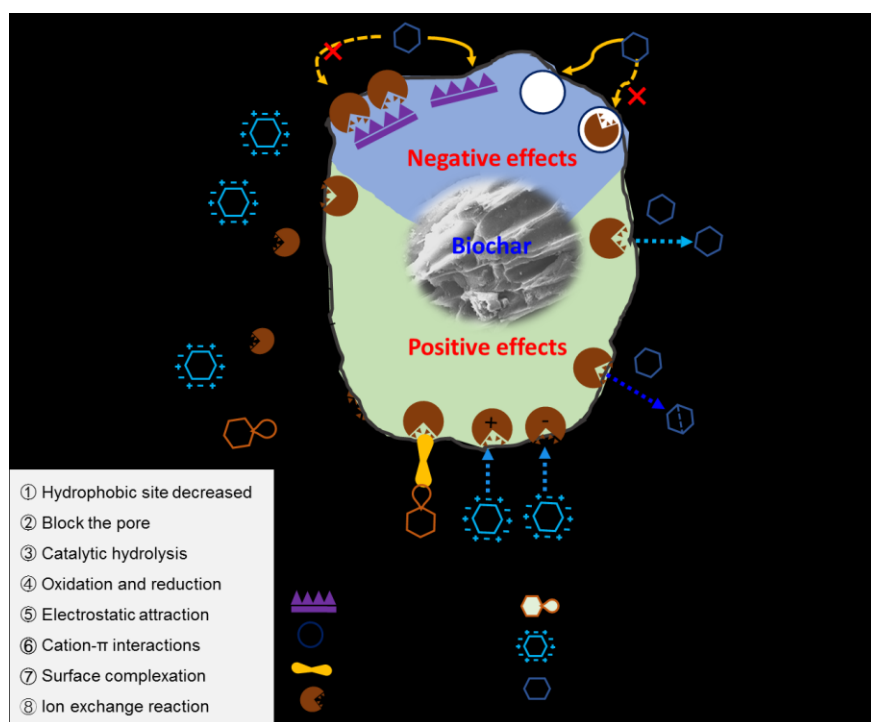
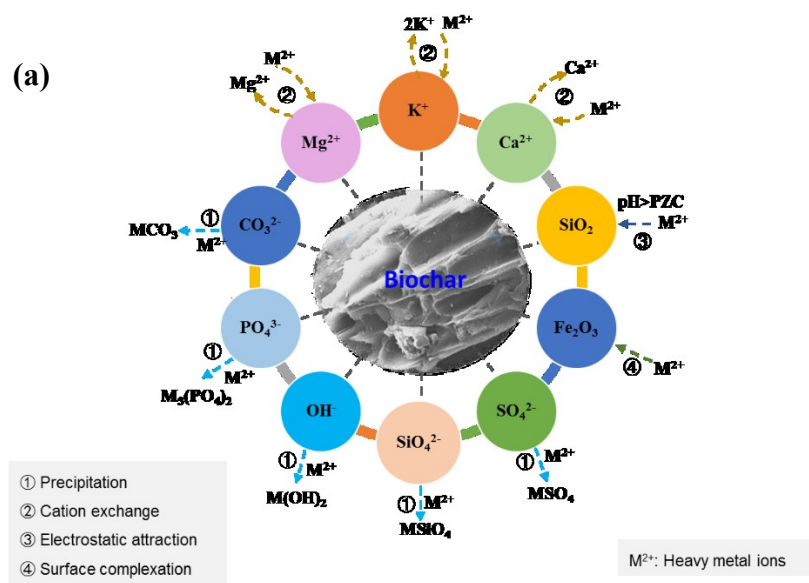


Fig. 2

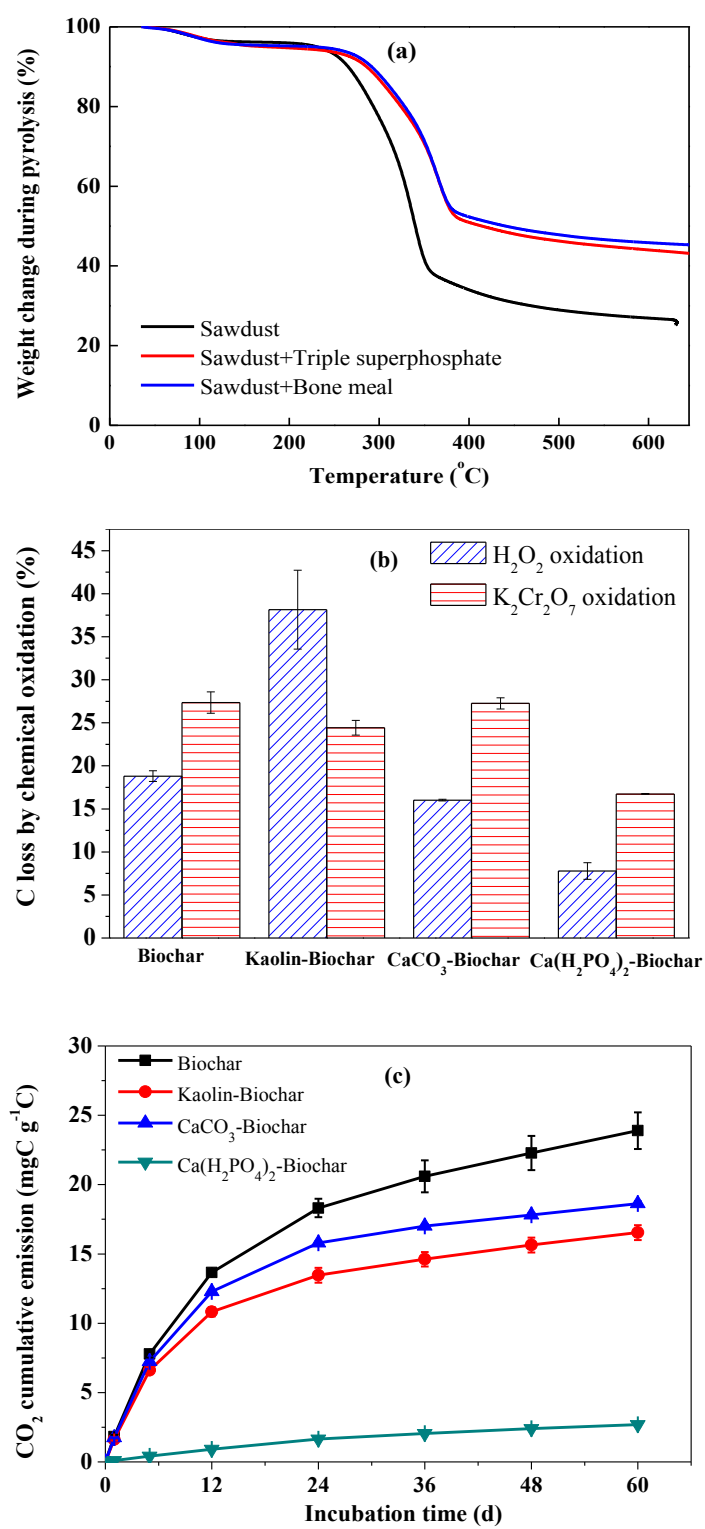


Fig. 3