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Review Application of biochar for the removal of pollutants from aqueous solutions

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HIGHLIGHTS

- This paper reviews recent findings on pollutants removal from water using biochar.
- Production and properties of biochar suggest that it can be a promising adsorbent.
- Biochar properties and circumambient conditions influenced the pollutants removal.
- Adsorption mechanisms depend on biochar properties and target pollutants.
- More studies are needed to close knowledge gaps before engineering application.

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ABSTRACT

In recent years, many studies have been devoted to investigate the application of biochar for pollutants removal from aqueous solutions. Biochar exhibits a great potential to efficiently tackle water contaminants considering the wide availability of feedstock, low-cost and favorable physical/chemical surface characteristics. This review provides an overview of biochar production technologies, biochar properties, and recent advances in the removal of heavy metals, organic pollutants and other inorganic pollutants using biochar. Experimental studies related to the adsorption behaviors of biochar toward various contaminants, key affecting factors and the underlying mechanisms proposed to explain the adsorption behaviors, have been comprehensively reviewed. Furthermore, research gaps and uncertainties that exist in the use of biochar as an adsorbent are identified. Further research needs for biochar and potential areas for future application of biochars are also proposed.

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1. Introduction

Biochar is a carbon-rich solid obtained by heating biomass, such as wood, manure with little or no oxygen (pyrolysis or "charring") (Sohi, 2012), which can be applied to soil for both agricultural gains and carbon sequestration. Biochar can slacken carbon release to the atmosphere from burning or degrading by carbon stabilization into a form resembling charcoal (carbon negative). By burying it in fields, it can store carbon in soil and improve soil properties. In addition, the bioenergy produced from pyrolysis process provides potential substitute for fossil fuels (carbon neutral) (Lehmann, 2007).

Publications which included the word "biochar" in the topic on indexed journals (according to ISI Web of Science™ from 2005 to 2013) have been growing steadily (Fig. 1), indicating a growing interest of the scientific community on biochar research. The increasing interest in biochar has inaugurated multidisciplinary areas for science researches and engineering applications. A large number of studies have highlighted the benefit of using biochar in terms of mitigating global warming, soil amendment, enhancing of crop yield and carbon storage (Whitman et al., 2011; Abit et al., 2012; Mao et al., 2012; Sohi, 2012; Khare and Goyal, 2013; Verheijen et al., 2014). Furthermore, there have also been considerable interests in using biochar to remove pollutants from aqueous solutions. The number of publications on indexed journals containing the keywords "biochar + water + adsorption" between 2005 and 2013 also increased notably, which accounts for approximately one-tenth of all "biochar" publications (Fig. 1).

The specific properties of biochar including large specific surface area, porous structure, enriched surface functional groups and mineral components make it possible to be used as proper adsorbent to remove pollutants from aqueous solutions. As an adsorbent, biochar has porous structure similar to activated carbon, which is the most commonly employed and efficient sorbent for the removal of diverse pollutants from water throughout the

world (Faria et al., 2004; Nakagawa et al., 2004; Chen et al., 2007). Compared with activated carbon, biochar appears to be a new potential low-cost and effective adsorbent. The production of activated carbon needs higher temperature and additional activation process. Comparatively, production of biochar is cheaper with lower energy requirements (Cao et al., 2009; Zheng et al., 2010; Karakoyun et al., 2011; Ahmad et al., 2012; Lu et al., 2012). The feedstocks of biochar production are abundant and low-cost, which mainly obtained from agricultural biomass and solid waste (Shen et al., 2012; Yao et al., 2012; Qian and Chen, 2013; Xu et al., 2013b). In addition, converting invasive plant into biochar can improve the invasive plant management and protect the environment (Dong et al., 2013). Therefore, the conversion of biomass into biochar as a sorbent is a "win-win" solution for both improving waste management and protecting the environment (Cao et al., 2009; Zheng et al., 2010).



Fig. 1. Evolution of the number of publications on indexed journals containing the keywords "biochar" and "biochar + water + adsorption" between 2005 and 2013. The pie graph shows the percentage of the available scientific literatures which concerned the removal of different pollutants using biochar.



Fig. 2. The benefits of biochar applied as an effective adsorbent for wastewater treatment.

Being a renewable resource and due to its economic and environmental benefits (Fig. 2), biochar is therefore a promising resource for environmental technology used for water contaminants treatment. Most studies have reported that biochar showed excellent ability to remove contaminants such as heavy metals, organic pollutants and other pollutants from aqueous solutions. Meanwhile, several biochars exhibit comparable or even better adsorption capacity than commercially activated carbon (Karakoyun et al., 2011; Xue et al., 2012; Zhang et al., 2012; Yang et al., 2014b). Specifically, biochar loaded with ammonium, nitrate, and phosphate also proposed to be a slow-release fertilizer to enhance soil fertility, as biochar after adsorption may contain abundance of valuable nutrients (Yao et al., 2011b, 2013b; Zhang et al., 2013c).

The available peer-reviewed scientific literatures about the biochar are mainly concerned about its application in soil, technical, economical, and climate-related aspects of biochar (Atkinson et al., 2010; Beesley et al., 2011; Duku et al., 2011; Jeffery et al., 2011; Lehmann et al., 2011; Meyer et al., 2011; Manyà, 2012; Ameloot et al., 2013; Gurwick et al., 2013; Stavi and Lal, 2013). However, very little review article describe the use of biochar for the removal of pollutants in water (Ahmad et al., 2013b). With the increasing interest of scientific research and future engineering applications of biochar for the purification of water and treatment of wastewater, an integrated understanding of biochar's function in aqueous solutions is urgently needed.

The specific aim of the present study is to review and analyze the published studies related to the application of biochar for the removal of contaminants from aqueous systems. This review (1) summarizes recent developments in the preparation and properties of biochar, and (2) describes the development of biochar as a sorbent material, as well as (3) discusses the adsorption mechanisms involved. As a result of this review process, the author's objectives are to highlight the further research needs for this exciting field of study, and direct attention to the novel research of biochar materials that may be applied into future projects involving the wastewater treatment.

2. Production and properties of biochar—a promising adsorbent

Biochar is carbon-rich, porous with oxygen functional groups and aromatic surfaces, and it exhibits differing physical and chemical properties depending on the feedstock and the pyrolysis technology. The feedstocks are mainly acquired from agricultural biomass, which is one of the most abundant renewable resources on the earth. A number of feedstocks, including crop residues, wood biomass, animal litters, and solid wastes have been utilized to produce biochar via various thermochemical processes (e.g., slow pyrolysis, fast pyrolysis, hydrothermal carbonization (HTC), flash carbonization, torrefaction and gasification) (Meyer et al., 2011). The list of solid biochar yields of different thermochemical processes and operating conditions is presented in Table S1.

2.1. Slow pyrolysis

The summaries of various biochars produced from different feedstocks and techniques that have been used to treat contaminated water are presented in Table 1. As can be seen, slow pyrolysis is the most commonly used technology for the wastewater treatment. This is because that, slow pyrolysis processes with a residence time of a few minutes to days are generally favored for biochar production (15–89%) (Table S1) (Tong et al., 2011; Yao et al., 2011a; Ahmad et al., 2012; Chen et al., 2012b).

Biochar's feedstocks (especially for plant biomass) are composed primarily of hemicellulose, cellulose and lignin (Rutherford et al., 2012), which are gradually pyrolyzed with the increase of temperature. Lignin is much more recalcitrant than hemicellulose and cellulose during charring (Rutherford et al., 2012). The pyrolysis characteristics were described via thermogravimetric and derivative thermogravimetric curve (TG-DTG) of raw biomass under anaerobic conditions (Fig. S1a) (Chen and Chen, 2009). The weight loss of drying process at low temperature is attributed to the evaporation of water. Subsequently, the major decomposition processes occurred between 200 and 500 °C (Chen and Chen, 2009; Shen et al., 2012; Chen et al., 2012b), and sequentially follow four steps: (i) the partial hemicellulose decomposition, (ii) the complete hemicellulose decomposition to partial cellulose decomposition, (iii) the full cellulose and partial lignin decomposition, and (iv) the successive decomposition and increasing degree of carbonization (Chen and Chen, 2009; Kumar et al., 2011; Rutherford et al., 2012; Shen et al., 2012; Chen et al., 2012b). After that, the weight loss in biochar became relatively gradual when the temperature was up to 700 °C. The yields of biochar were approximately 15-90% by different feedstocks and decomposition processes, and reduced with the increase in temperature. While, nearly 15-25% of biochar still remained even temperature up to 700 °C (Ahmad

 Table 1

 The application of biochar produced from different feedstocks and techniques in aqueous solutions.

Biomass feedstocks	Pyrolytic temperature (°C)	Residence time	Pyrolysis techniques	Contaminants	References
Bamboo	450, 600	_	Slow pyrolysis	Sulfamethoxazole	Yao et al. (2012)
Brazilian pepper wood	450, 600	-	Slow pyrolysis	Sulfamethoxazole	Yao et al. (2012)
Cattle manure	100-700	6 h	Slow pyrolysis	Aluminum	Qian and Chen (2013)
Coconut coir	250-600	1 h	Slow pyrolysis	Chromium	Shen et al. (2012)
Corn straw	600	2 h	Slow pyrolysis	Copper and zinc	Chen et al. (2011)
Dairy manure	200, 350	4 h	Slow pyrolysis	Lead and atrazine	Cao et al. (2009)
Dairy manure	350	4 h	Slow pyrolysis	Pb, Cu, Zn, and Cd	Xu et al. (2013b)
Eucalyptus	400	30 min	Slow pyrolysis	Methylene blue dye	Sun et al. (2013b)
Giant reed	300-600	2 h	Slow pyrolysis	Antibiotic sulfamethoxazole	Zheng et al. (2013)
Grass	200-600	1 h	Slow pyrolysis	Fluorinated herbicides	Sun et al. (2011)
Hardwood	450	<5 s	Fast pyrolysis	Copper and zinc	Chen et al. (2011)
Hickory wood	450, 600	-	Slow pyrolysis	Sulfamethoxazole	Yao et al. (2012)
Miscanthus sacchariflorus	300-600	1 h	Slow pyrolysis	Cadmium	Kim et al. (2013)
Orange peel	400-700	2 h	Slow pyrolysis	Fluoride	Oh et al. (2012)
Orange peel	300, 700	6 h	Slow pyrolysis	Hydrophobic organic compounds (HOCs)	Chen et al. (2012c)
Orange peel	150-700	6 h	Slow pyrolysis	Naphthalene and 1-naphthol	Chen and Chen (2009)
Palm bark	400	30 min	Slow pyrolysis	Methylene blue dye	Sun et al. (2013b)
Peanut shells	300, 700	3 h	Slow pyrolysis	Trichloroethylene	Ahmad et al. (2012)
Pine needle	300-700	3 h	Slow pyrolysis	Trichloroethylene	Ahmad et al. (2013a)
Pine needle	300, 700	6 h	Slow pyrolysis	Hydrophobic organic compounds (HOCs)	Chen et al. (2012c)
Pine needle litters	100-700	6 h	Slow pyrolysis	Naphthalene (NAPH), nitrobenzene (NB),	Chen et al. (2008)
				and m-dinitrobenzene (m-DNB)	
Pine wood shavings	150-700	6 h	Slow pyrolysis	Naphthalene	Chen et al. (2012b)
Pinewood	300	20 min	Hydrothermal carbonization (HTC)	Lead	Liu and Zhang (2009)
Rice husk	300	20 min	Hydrothermal carbonization (HTC)	Lead	Liu and Zhang (2009)
Rice husk	350	4 h	Slow pyrolysis	Pb, Cu, Zn, and Cd	Xu et al. (2013b)
Rice straw	100-700	6 h	Slow pyrolysis	Aluminum	Qian and Chen (2013)
Sludge	400-700	2 h	Slow pyrolysis	Fluoride	Oh et al. (2012)
Soybean stover	300, 700	3 h	Slow pyrolysis	Trichloroethylene	Ahmad et al. (2012)
Spartina alterniflora	400	2 h	Slow pyrolysis	Cu(II)	Li et al. (2013a)
Sugar beet tailings	600	2 h	Slow pyrolysis	Phosphate	Yao et al. (2011a)
Sugarcane bagasse	450, 600	-	Slow pyrolysis	Sulfamethoxazole	Yao et al. (2012)
Sugarcane bagasse	300, 700	6 h	Slow pyrolysis	Hydrophobic organic compounds (HOCs)	Chen et al. (2012c)
Swine manure	400	1 h	Slow pyrolysis	Herbicide paraquat	Tsai and Chen (2013)
Switchgrass	300	30 min	Hydrothermal carbonization (HTC)	U(VI)	Kumar et al. (2011)
Wood	200-600	1 h	Slow pyrolysis	Fluorinated herbicides	Sun et al. (2011)

et al., 2012, 2013a; Oh et al., 2012; Chen et al., 2012b; Qian and Chen, 2013), which confirmed the thermal stability of biochar as an adsorbent.

The elemental compositions of biochar changes with pyrolytic temperature. Summary of the physico-chemical properties of biochar applied in aqueous systems is shown in Table S2. The results of various studies demonstrate that carbon content tends to be enhanced with increasing pyrolytic temperature. Conversely, nitrogen, hydrogen and oxygen content decreased as the pyrolytic temperature increased (Ahmad et al., 2012; Li et al., 2013b). However, Kim et al. (2013) and Harvey et al. (2011) found that nitrogen distribution in the biochars varied with different plant species but was largely unaffected by biochar formation temperature. The increase of carbon content and decrease of hydrogen and oxygen content resulting in a decrease of H/C, O/C and (O + N)/C molar ratios as the pyrolytic temperature increased (Table S2). Van Krevelen diagram has been used to depict the changes of elemental ratios with temperatures (Keiluweit et al., 2012; Li et al., 2013b). Van Krevelen plot of elemental ratios for rice straw and sawdust derived biochars prepared at various charring temperatures is shown in Fig. S1b (Li et al., 2013b). The H/C ratio has been used as a representative for the degree of carbonization as H is primarily associated with the organic matter in biomass. The surface hydrophilicity of biochar may be described by the molar oxygen to carbon (O/C) ratio since it is indicative of polar-group content (Chun et al., 2004; Chen et al., 2011). The lower O/C ratio indicated that the surfaces of biochar were more aromatic and less hydrophilic due to higher extent of carbonization and loss of polar functional

groups at higher temperature (Chen et al., 2008, 2012c; Ahmad et al., 2012; Kim et al., 2013). The decreased ratios of (O + N)/C, which serves as an indicator of polarity, reflects a decrease of polar-group content with the increase of pyrolytic temperature (Ahmad et al., 2012; Chen et al., 2012b,c).

Surface chemical composition plays an important role in the adsorption property of biochar (Pintor et al., 2012). The chemical characteristics of the biochar surface are intimately connected to its chemical composition. Overall, the Fourier transformed infrared (FTIR) results demonstrate qualitative differences in the surface functional groups of biochar due to both differences in the original feedstocks and the pyrolysis conditions (Kumar et al., 2011). Pyrolytic temperature had considerable influence on the surface functional groups of biochars, leading to a decrease in most bands as pyrolytic temperature increased (Figs. S1c and S1d) (Chen et al., 2011, 2012a; Kim et al., 2013; Uchimiya et al., 2013). Table S3 summarizes the surface chemical structures of biochars based on the corresponding peaks of FTIR spectra. The band corresponding to the various surface groups/structure peaks decreased (such as -OH stretching at 3400 cm^{-1} , aliphatic chain -CH₂ and -CH₃ stretching at 2940 cm⁻¹ and aromatic CO— and phenolic —OH stretching at 1270 cm⁻¹) during the pyrolysis process, which might be due to the increase in the pyrolysis reaction of different constituent in biomass (Chen et al., 2012a). Further, Uchimiya et al. (2013) reported that the peak attributed to C=O stretching of phenolic esters and lactones at 1700 cm⁻¹, and aromatic C=C and C=O stretching of conjugated ketones and quinones at 1600 cm⁻¹ increased and then decreased with the increase of temperature.

These FTIR spectra agree with the changes in elemental composition and the decomposition process of the raw biomass in TG–DTG, indicating that increasing pyrolytic temperature produces biochar with the decreases in surface acidity and polarity, and the increase in aromaticity (Ahmad et al., 2012, 2013a; Kim et al., 2013; Uchimiya et al., 2013).

Structural and compositional changes in biochars are also accompanied by changes in their surface properties (Harvey et al., 2011). A higher O/C ratio in a biochar material may indicate the presence of more functional groups (such as hydroxyl, carboxylate, and carbonyl) that could contribute to a higher cation exchange capacity (CEC) value for the biochar (Lee et al., 2010; Yuan et al., 2011). CEC represents the negative surface charge of the biochars (Xu et al., 2011; Jiang et al., 2012). For a given biomass feedstock, CEC might increase and then decrease with the increase of pyrolytic temperature, which is correlated well with the occurrence of functional groups on biochar (Harvey et al., 2011). This correlation suggests that the pyrolysis of biomass is account for the generation of biochar surface charge. Harvey et al. (2011) studied the CEC of different biochars pyrolyzed from cordgrass, honey mesquite, and loblolly pine at four temperatures, and the results showed that the CEC of these biochars increased and then decreased with the increase of pyrolytic temperature. For instance, the CEC of loblolly pine biochar increased from 16.5 cmol kg⁻¹ (pyrolyzed at 200 °C) to 23.8 cmol kg⁻¹ (at 350 °C) and then decreased to 2.1 cmol kg⁻¹ (at 650 °C). The lower CEC values observed at higher pyrolytic temperatures may be attributed to the subsequent aromatization of biochars and the release of functional groups on biochar.

As shown in Table S2, the Brunauer–Emmett–Teller (BET) surface areas increased with increasing pyrolytic temperature due to the escape of volatile substances such as cellulose and hemicelluloses and the formation of channel structures during pyrolysis (Ahmad et al., 2012; Chen et al., 2012c; Kim et al., 2013). The release of volatile components facilitated the formation of vascular bundles structure in biochar and thus improved the specific surface area and pore structure of biochar (Li et al., 2013a). A decrease of pore size, formation of internal pore structures, and an increase in porosity as a result of volatiles release during carbonization could also be observed in biochars (Ahmad et al., 2012).

Additionally, pH values indicated that most biochars produced from slow pyrolysis are alkaline (Table S2). Adding biochar into deionized water largely increased solution pH and biochar produced at higher temperatures exhibited a higher pH. The increase of pH is likely resulted from the release of alkali salts from feedstock during the pyrolysis process (Ahmad et al., 2012; Kim et al., 2013). The change of biochar pH is consistent with the Boehm titration results, which indicated that total acidity in the biochars decreased, while total basicity increased remarkably with increasing pyrolytic temperature (Ahmad et al., 2013a).

Based on the current studies described in the literatures, pyrolytic temperature plays a significant role in changing biochar characteristics. Biochar produced at higher temperature showed high pH, CEC and surface area. However, biochar produced at low temperature contained more actives sites and existed stable carbonoxygen complexes (Kumar et al., 2011). The pyrolytic temperature is believed to have a profound effect on physic-chemistry properties of the resultant char and likely a major parameter contributing to the adsorption properties of biochar.

In conclusion, the properties analysis results point out that biochar can be used as an effective adsorbent for contaminants treatment. However, a number of issues must be concerned to make the concept valid. It is certain that there are a range of key parameters affecting the characteristics of biochar product. And these factors can have conspicuous influence on the adsorption efficiency of resulting biochar correspondingly. Further studies we should provide insight into optimum formation conditions to produce biochar with the best properties, so as to simultaneously enhance adsorption ability and provide long-term carbon sequestration.

2.2. Hydrothermal carbonization

Hydrothermal carbonization (HTC) was also utilized by several studies to produce biochar for pollutants removal (Table 1). Hydrothermal carbonization (HTC) usually pyrolyze the biomass at 180-300 °C in water for 30 min to 16 h, resulting in 36-72% biochar yield (Table S1) (Rillig et al., 2010; Hoekman et al., 2011; Mumme et al., 2011; Kalderis et al., 2014). Most studies about HTC were concerned with its use for making energy-dense solid fuel from lignocellulosic biomass (Liu et al., 2013; Reza et al., 2013: Yan et al., 2014). Meanwhile, many studies also attempted to use biochar produced from HTC to removal the pollutants from aqueous solutions (Liu and Zhang, 2009; Kumar et al., 2011; Regmi et al., 2012; Zhang et al., 2013d). Using HTC process to produce biochar from lignocellulosic biomass is getting more and more attention due to its inherent advantage of using wet biomass (Kumar et al., 2011). Irregular surface and much more oxygen-containing groups are developed after hydrothermal treatment, which is significantly important for biochar as an adsorbent (Liu and Zhang, 2009).

Slow pyrolysis and hydrothermal carbonization are two of the most efficient thermochemical technologies to produce biochar in terms of its wide range of feedstocks and high carbon yield. Compared with slow pyrolysis, the HTC method uses less energy and can use unconventional wet biomass sources (e.g., sewage sludge, city wastes, animal and human excreta) without requiring drying process (Malghani et al., 2013). In addition, biochars produced through HTC have much higher oxygen functional groups and higher CEC than the biochars produced by slow pyrolysis (Liu and Zhang, 2009; Huff et al., 2014). It is reported that the majority of biochars produced by hydrothermal carbonization were more acidic than biochars produced by pyrolysis (Fuertes et al., 2010; Kumar et al., 2011; Kalderis et al., 2014). The lower pH could be attributed to the existence of more acid functional groups such as carboxyl, lactone, and phenol (Xu et al., 2013a). Temperature is also the main influencing factor for the properties of biochar produced from HTC. Higher temperatures increased the char's carbon content but decreased its yield, volatile matter content, ion exchange capacity, O-containing functional groups and surface area (Mumme et al., 2011; Kang et al., 2012). The appropriate properties of biochar produced by HTC make it possible to be used as an adsorbent. Biochars produced by HTC even reported to have better removal efficiency than slow pyrolysis in some case (Liu et al., 2010; Elaigwu et al., 2013). However, the HTC-biochar was readily biodegradable, whereas slow pyrolysis biochar is more stable and thus had markedly higher potential for carbon sequestration than HTC (Bai et al., 2013; Malghani et al., 2013).

2.3. Other thermochemical technologies

However, there is little information about flash carbonization, torrefaction, fast pyrolysis and gasification that were used to treat contaminated water. This is because that these technologies are generally favored for bio-oil, solid fuel or synthetic gas yields. Flash carbonization transforms biomass into gas at elevated pressure (at about 1–2 MPa). The reaction time of the process is below 30 min, and the temperature is in the range of 300–600 °C (Antal et al., 2003; Meyer et al., 2011). Torrefaction typically involves slow heating in the temperature range of 250–300 °C, which releases both

moisture and carbon dioxide from the biomass, resulting in a solid fuel with a lower O/C ratio (Pimchuai et al., 2010). Fast pyrolysis usually uses short residence time (≤ 2 s) and the peak temperature is set between 300 and 1000 °C in order to obtain the highest bio-oil yield, but inhibit the formation of charcoal (Mohan et al., 2006; DeSisto et al., 2010; Manyà, 2012; Shah et al., 2012). In gasification processes, the biomass is converting into gases in the gasification chamber at high temperature (700–800 °C) at atmospheric or elevated pressure (Brewer et al., 2009; Lee et al., 2010).

As shown in Table S1, the solid biochar yields obtained from fast pyrolysis and gasification processes are significantly lower as compared to that of slow pyrolysis, flash carbonization, hydrothermal, carbonization and torrefaction. Although the solid biochar is not the main/target products of flash carbonization, torrefaction, fast pyrolysis and gasification, the biochars obtained as the by-product of these processes may also have high adsorption ability for pollutants. So that the further use of biochar produced by other thermochemical technologies cannot be underestimated.

3. Application of biochar for water treatment

The large specific surface area, porous structure, surface functional groups of biochars are the important features promising their high removal efficiencies of contaminants. In the past few years, many reports on adsorption of various contaminants on biochar have been published. The contaminants include heavy metals, organic pollutants and other pollutants. According to the available literatures about biochar application in water treatment, nearly 46% of the studies concerned the removal ability of biochar for heavy metals, 39% for organic pollutants, 13% for NP, and 2% for other pollutants (Fig. 1).

3.1. Adsorption isotherm

The contamination of toxic metals in aqueous solutions has become a pervasive problem throughout the world. Thus, the

Table 2

Adsorption characteristics of	various heavy	metals with	biochars.
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focuses of research on the application of biochar for water treatment. Adsorption characteristics of biochars exposed to various heavy metals are presented in Table 2. The concerned heavy metals include aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), uranium (U), and zinc (Zn). Adsorption isotherm is essential in optimizing the use of adsorbents because it describes how adsorbates interact with adsorbents (Goh et al., 2008). A number of empirical models have been employed to analyze experimental data and describe the equilibrium of heavy metals adsorption onto biochars. The most popular and widely used of these are: Langmuir, Freundlich, Langmuir-Freundlich and Temkin equations. As evidenced by the collected data, both Langmuir and Freundlich model fit the data better than other equations when used to describe the equilibrium adsorption of heavy metals by biochars (Table 2). And the results vary widely depending on the properties of biochar and the target heavy metals. The Langmuir isotherm assumes monolayer adsorption of adsorbate on a homogeneous surface of adsorbent (Hu et al., 2011). Chen et al. (2011) studied the Cu(II) and Zn(II) adsorption isotherms at different initial heavy metal concentrations ranging from 0.1 to 5.0 mM. The resulting correlation coefficients suggested that the Langmuir model ($R^2 > 0.998$) fit the data better than the Freundlich model (R^2 were 0.86–0.94). Tong et al. (2011) used Langmuir, Freundlich and Temkin equations to fit the adsorption data of Cu(II) for three biochars. The corresponding correlation coefficients (R^2) indicated that the Langmuir equation gave the best fit. Several studies also reported that the dynamic data regarding heavy metal adsorption by biochar fits better to Freundlich than Langmuir isotherm (Table 2) (Lu et al., 2012; Zhang et al., 2013c; Agrafioti et al., 2014; Yang et al., 2014a). Freundlich isotherm reveals information regarding the heterogenous adsorption and is not restricted to the formation of a monolayer (Hu et al., 2011; Kim et al., 2013). In the study of Pb(II) and Cr(VI) adsorption by biochar pyrolyzed from the municipal wastewater sludge, adsorption isotherms on the biochar were simulated with

removal of heavy metals has been becoming one of the main

Feedstock	Pyrolytic temperature (°C)	Residence time	Heavy metal	Adsorption temperature (°C)	Adsorption pH	$Q_{\rm max} ({ m mg}{ m g}^{-1})$	Isotherm	Kinetic model	References
Canola straw	400	3.75 h	Cu(II)	25 ± 1	5.0	0.59 ^a	Langmuir	-	Tong et al. (2011)
Cattle manure	100	6 h	Al	25 ± 1	4.3	0.2424 ± 15.0^{a}	Langmuir	-	Qian and Chen (2013)
Cattle manure	400	6 h	Al	25 ± 1	4.3	0.2963 ± 6.2^{a}	Langmuir	-	Qian and Chen (2013)
Cattle manure	700	6 h	Al	25 ± 1	4.3	0.2432 ± 4.0^{a}	Langmuir	-	Qian and Chen (2013)
Corn straw	600	2 h	Cu(II)	22 ± 2	5	12.52	Langmuir	PSO ^b	Chen et al. (2011)
Corn straw	600	2 h	Zn(II)	22 ± 2	5	11.0	Langmuir	PSO	Chen et al. (2011)
Hardwood	450	<5 s	Cu(II)	22 ± 2	5	6.79	Langmuir	PSO	Chen et al. (2011)
Hardwood	450	<5 s	Zn(II)	22 ± 2	5	4.54	Langmuir	PSO	Chen et al. (2011)
Miscanthus sacchariflorus	300	1 h	Cd(II)	25	7	11.40 ± 0.47	Langmuir	PSO	Kim et al. (2013)
Miscanthus sacchariflorus	400	1 h	Cd(II)	25	7	11.99 ± 1.02	Freundlich	PSO	Kim et al. (2013)
Miscanthus sacchariflorus	500	1 h	Cd(II)	25	7	13.24 ± 2.44	Freundlich	PSO	Kim et al. (2013)
Miscanthus sacchariflorus	600	1 h	Cd(II)	25	7	12.96 ± 4.27	Freundlich	PSO	Kim et al. (2013)
Peanut straw	400	3.75 h	Cu(II)	25 ± 1	5.0	1.40 ^a	Langmuir	-	Tong et al. (2011)
Pine needles	200	16 h	U(VI)	25	-	62.7	Langmuir	PSO	Zhang et al. (2013d)
Pinewood	300	20 min	Pb(II)	25	-	3.89	Langmuir	PSO	Liu and Zhang (2009)
Rice husk	300	20 min	Pb(II)	25	-	1.84	Langmuir	PSO	Liu and Zhang (2009)
Rice straw	100	6 h	Al	25 ± 1	4.3	0.1309 ± 16.0 ^a	Langmuir	-	Qian and Chen (2013)
Rice straw	400	6 h	Al	25 ± 1	4.3	0.3976 ± 11.0 ^a	Langmuir	-	Qian and Chen (2013)
Rice straw	700	6 h	Al	25 ± 1	4.3	0.3537 ± 8.2 ^a	Langmuir	-	Qian and Chen (2013)
Sludge	550	2 h	Pb(II)	25	-	-	Freundlich	PSO	Lu et al. (2012)
Sludge	400	2 h	Pb(II)	25 ± 2	5.0	-	Langmuir	PSO	Zhang et al. (2013c)
Sludge	400	2 h	Cr(VI)	25 ± 2	5.0	-	Freundlich	PSO	Zhang et al. (2013c)
Soybean straw	400	3.75 h	Cu(II)	25 ± 1	5.0	0.83 ^a	Langmuir	-	Tong et al. (2011)
Spartina alterniflora	400	2 h	Cu(II)	25	6.0	48.49 ± 0.64	Langmuir	PSO	Li et al. (2013a)
Sugar beet tailing	300	$\sim 2 h$	Cr(VI)	22 ± 0.5	2.0	123	Langmuir	PSO	Dong et al. (2011)
Switchgrass	300	30 min	U(VI)	25	3.9 ± 0.2	2.12	Langmuir	-	Kumar et al. (2011)

^a mmol g^{-1} .

^b Pseudo-second-order.

Langmuir and Freundlich equations. The results showed that Pb(II) adsorption behavior fitted better with Langmuir equations, whereas Cr adsorption isotherm was found to better fit with Freundlich equations (Zhang et al., 2013c). Lead sorption by sludgederived biochar were investigated by Lu et al. (2012), and the results showed that Pb(II) sorption isotherm was well fitted with Freundlich equation.

Biochar also showed high affinity for organic pollutants. In the past few years, many laboratory experiments were performed to investigate the potential of biochar as an adsorbent for removing organic contaminants from aqueous solution. Overall, the results from these studies demonstrated that the biomass derived char can be used as a low-cost adsorbent for removal of environmental organic pollutants from the water environment. The contaminants include dyes, pesticides, herbicides, antibiotics, and other organic contaminants. The characteristics of organic contaminants adsorption by biochars are presented in Table 3. The adsorption of organic contaminants by biochar also showed the perfect fit of the experimental data with the Langmuir or Freundlich isotherm model. For instance, Ahmad et al. (2012) used crop residues derived biochars to removal trichloroethylene (TCE) from water. The results showed that the Langmuir model had a good description of the TCE adsorption on biochars based on the correlation coefficients. The study of cationic methylene blue dye adsorption on different biochars got the same conclusion (Sun et al., 2013b). However, Yao et al. (2013a) investigated the adsorption of fluoroquinolone antibiotics using sludge-derived biochar made of various wastewater sludge. The results showed that Freundlich model gave the best fit with the experimental data of all the produced biochar.

Apart from heavy metals and organic contaminants, other pollutants such as ammonium/nitrate (Zhang et al., 2012; Hale et al., 2013; Hollister et al., 2013), phosphate (Yao et al., 2011b, 2013b; Hollister et al., 2013; Zhang and Gao, 2013; Zhang et al., 2013a), fluoride (Oh et al., 2012) and perchlorate (Fang et al., 2013) were also investigated. Biochar was evaluated for ammonium, nitrate, and phosphate removal from aqueous solution to quantify its potential for nutrient pollution mitigation in aquatic ecosystems (Hale et al., 2013; Hollister et al., 2013). Yao et al. (2013c) used an engineered biochar prepared from Mg-enriched tomato tissues to reclaim and reuse phosphate from aqueous solution. Their results suggested that the NP-loaded biochar can be applied to soils as an effective slow-release P-fertilizer. Similarly, Hale et al. (2013) confirmed that biochar can add and slowly release essential nutrients to soil and thus improve agricultural properties. The biochars used for adsorption of PO₄-P and NH₄-N

Table 3				
Adsorption chara	acteristics of vari	ous organic cor	ntaminants with	biochars

were able to release NP for crops use. As the widespread applications of engineered nanoparticles (ENPs) and the potential toxic effect of ENPs to the aqueous environment and ecosystem, Inyang et al. (2013) applied biochar to remove three ENPs: silver nanoparticles (AgNPs), carbon nanotubes (CNTs), and titanium dioxide (NTiO₂) from water, which indicated that biochar can be used as a low-cost filter material to remove ENPs. Furthermore, concerning its favorable physicochemical properties, biochar can be used for further other contaminants removal, e.g. oxyanions, pathogenic bacteria, and endocrine disrupting compounds (EDCs).

3.2. Adsorption kinetics

Adsorption kinetics displays a strong relationship with the physical and/or chemical characteristics of the biochar. The result of adsorption kinetics influences the adsorption mechanism, which may involve mass transport and chemical reaction processes (Kołodyńska et al., 2012; Boutsika et al., 2014). For a practical application of biochar in pollutant removal, knowledge of the kinetics of this process is required. Three most popular kinetic models have been used to study the adsorption of contaminants by biochars: the pseudo-first-order kinetic model, the pseudo-second-order kinetic model provide the valuable information which controlled the adsorption process involving adsorbent surface, chemical reaction, and/or diffusion mechanisms (Reddy and Lee, 2013).

Most of studies used the pseudo-first-order and pseudo-second-order kinetic models to study the adsorption of water pollutants onto biochars. The summaries of best fit of kinetic model for removal of contaminants using various biochars were shown in Tables 2 and 3. As evidenced by the data shown in Tables 2, the removal processes of heavy metals were well followed pseudo-second-order model in most cases. The pseudo-secondorder kinetic model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through the sharing or exchange of electrons between adsorbent and adsorbate (Ho and McKay, 1999). For instance, Lu et al. (2012) studied the kinetics of Pb²⁺ adsorption on sludge-derived biochar at initial pH 2.0-5.0. This kinetics was found to be well fitted by the pseudo-second-order model, which assumes chemisorption of the adsorbate on the adsorbent. Liu and Zhang (2009) applied both pseudo-first-order and pseudo-second-order models to study the lead adsorption mechanism onto pinewood and rice husk derived biochars, and reported a similar results. Kołodyńska et al. (2012) selected Cu(II) and Pb(II) ions

Feedstock	Pyrolytic temperature (°C)	Residence time	Contaminants	Adsorption temperature (°C)	Qmax (mg g ⁻¹)	Isotherm	Kinetic model	References
Canola straw Eucalyptus Kenaf fiber Maize straw Palm bark Peanut shells Peanut shells Peanut straw Rice hull Soybean stover Soybean stover Soybean staw Swine manure Wastewater sludges	350 400 1000 300 400 300 700 350 350 350 350 350 350 350 350 350 3	4 h 30 min - 1.5 h 30 min 3 h 3 h 4 h 3 h 3 h 4 h 3 h 1 h 1 h	Methyl violet Methylene blue dye Oxytetracycline Methylene blue dye Trichloroethylene Trichloroethylene Methyl violet Methyl violet Trichloroethylene Trichloroethylene Methyl violet Paraquat Eluoroquinolone	$25 \pm 1 \\ 40 \\ 30 \\ 25 \pm 0.5 \\ 40 \\ 25 \\ 25 \\ 25 \pm 1 \\ 25 \\ 25 \\ 25 \\ 25 \\ 25 \\ 25 \\ 25 \\ 25$	$\begin{array}{c} (110 \text{ g} \text{ g}) \\ \hline \\ - \\ 2.06 \\ 18.18 \\ - \\ 2.66 \\ 12.12 \\ 32.02 \\ 256.4^{a} \\ 123.5^{a} \\ 123.5^{a} \\ 12.48 \\ 31.74 \\ 178.6^{a} \\ 14.79 \\ 19.80 \pm 0.40 \end{array}$	Langmuir Langmuir Freundlich Langmuir Langmuir Langmuir Langmuir Langmuir Langmuir Langmuir Langmuir Freundlich	- PSO PSO PSO - - - - - - - PSO - - - - - - -	Xu et al. (2011) Sun et al. (2013b) Mahmoud et al. (2012) Jia et al. (2013) Sun et al. (2013b) Ahmad et al. (2012) Ahmad et al. (2012) Xu et al. (2011) Ahmad et al. (2012) Ahmad et al. (2012) Xu et al. (2011) Tsai and Chen (2013) Yao et al. (2013)
wastewater sludges	550	IN	antibiotics	25 ± 2	19.80 ± 0.40	Freundlich	-	Yao et al. (2013a)

^a mmol kg⁻¹.

^b Pseudo-second-order.

for studies of kinetic and adsorptive characterization of biochar in metal ions removal. The kinetic data showed that the kinetic process was also fitted well to the pseudo-second-order model. Khare et al. (2013) used plant waste derived biochar for removal different metals (Cd, Cr, Cu and Pb) from acidic solutions, and their results showed that the adsorption of metal ions can be described more appropriately by the pseudo-second-order kinetics model than the first-order kinetic model, which suggested that the rate limiting step may be the chemical adsorption.

It is noted that pseudo-second-order model fitted well to the kinetic data for the most studied metal ions rather than pseudo-first-order. Furthermore, most studies related organic contaminants adsorption onto biochars also followed pseudo-second-order model indicating chemisorption process (Table 3). Jia et al. (2013) investigated the sorption of oxytetracycline from aqueous solution to maize-straw-derived biochar, and the resulted date fitted well into the pseudo-second-order kinetics model. Sun et al. (2013b) also reported that pseudo-second-order kinetics was the most suitable model for describing the adsorption of methylene blue dye onto the biochars prepared from anaerobic digestion residue, palm bark and eucalyptus.

3.3. Factors affecting adsorption of contaminants on biochar

The adsorption efficiency of biochar tend to be influenced by properties of biochar, deashing treatment, pH, dosage of adsorbent, competitive anions, and temperature. Here we have outlined the above mentioned factors that influenced the contaminants removal in the aqueous systems.

3.3.1. Properties of biochar

As described before, the pyrolytic temperature, residence time, feedstock, and thermochemical conversion technology have profound effects on the properties of biochar. Correspondingly, it is obvious that these factors may have conspicuous influence on the adsorption efficiency toward various pollutants. Of which, temperature is presumably a key parameter. It was found that the pyrolytic temperature had more influence on structural characteristics and isotherms shape of the biochar than the biomass feedstocks (Chen et al., 2012c). Chen et al. (2008) assessed the combined adsorption and partition effects of biochars produced by pyrolysis of pine needles at different temperatures (100-700 °C). The results turned out that the pyrolytic temperature significantly altered the structures of biochars, and played an important role in the adsorption of various organic contaminants. The contribution of adsorption increased in the order of increasing temperature, which is consistent with their specific surfaces (Chen et al., 2008). Chen et al. (2012b) stated that the pyrolytic temperature of a biomass affected the rate of uptake of a compound by a biochar because the temperature affected the degree of carbonization of a biochar. At higher temperature, the organic matters of the biomass were completely carbonized, the surface area was greatly increased, and more nanopores were developed, resulting in the sharply enhanced adsorption rate of Naphthalene (NAP). Similar conclusions of greater adsorption capacity with higher pyrolytic temperature were also drawn by Zhou et al. (2010) and Ahmad et al. (2013a). Ahmad et al. (2013a) found that the presence of more carbonized matters in the biochars produced at high pyrolytic temperatures caused greater adsorption of trichloroethylene (TCE). The removal of the oxygen and hydrogen carrying functional groups with increasing pyrolytic temperature induced the increase in the hydrophobicity of biochars, resulting in the enhancement of the relatively hydrophobic TCE adsorption.

Most reports have drawn the same conclusions: increasing of pyrolytic temperature took an active role in the adsorption of organic contaminants. In essence, the pyrolytic temperature was also reported have effects on the adsorption of heavy metals. Kim et al. (2013) reported that the pyrolytic temperature significantly influenced the structural, elemental and morphological properties of biochars. As a result, pH and surface area of biochar increased greatly at pyrolytic temperatures > 500 °C, resulting in the increase of Cd adsorption capacity with increasing pyrolytic temperature. However, Shen et al. (2012) stated that the Cr(VI) removal capacity decreased as the pyrolytic temperature increased. Cr(VI) removal by coconut coir biochar was primarily attributed to the reduction of Cr(VI) to Cr(III) by the materials, which was determined by the type and amount of oxygen-containing functional groups of the materials rather than by their surface areas. Increase of the pyrolytic temperature added more surface areas of the chars, while the number of oxygen-containing functional groups of the chars decreased, resulting in the decrease of adsorption. Similar results were also reported in the study of lead sorption by bagasse biochars. The maximum sorption capacity of Pb by bagasse biochars decreased from 21 to 6.1 mg g^{-1} as temperature increased from 250 to 600 °C due to the release of oxygencontaining surface groups during charring at high temperature (Ding et al., 2014).

The adsorption capability of biochar was also significantly influenced by the natural compositions of feedstock. Given the same pyrolysis condition, the adsorption capacity of biochars for contaminants varied with the types of raw biomass (Sun et al., 2014). The removal ability varies with different biochar feedstock sources as the mineral components (such as CO_3^{2-} , PO_4^{3-}) originated from the feedstocks play an important role in the adsorption properties of biochar (Cao et al., 2009; Xu et al., 2013b,c). Xu et al. (2011) investigated the adsorption of methyl violet by the biochars from four crop residues. They found that the adsorption capacity varied with their feedstock in the following order: canola straw char > peanut straw char > soybean straw char > rice hull char, which was generally consistent with the amount of negative charge of the biochars. Xu et al. (2013b) reported that dairy manure biochar was more effective than rice husk biochar in removing Pb. Cu. Zn. and Cd from both mono and multi-metal solutions. The biochars came from the co-pyrolysis of biomass were also used to tackle contaminants. Bernardo et al. (2013) investigated biochars from the co-pyrolysis of pine, used tires and plastic wastes for the removal of Pb²⁺ from aqueous medium. However, they concluded that mixing the three raw materials for pyrolysis did not improve the removal efficiency of Pb^{2+} by the resulting char.

Several researchers further compared the adsorption properties of biochar produced via different pyrolysis processes. Liu et al. (2010) stated that the hydrothermal treatment created much more oxygen-containing groups on biochar surface than pyrolysis process. Similarly, Kumar et al. (2011) concluded that the biochar produced from hydrothermal carbonization (HTC) showed better adsorption properties for copper removal from wastewater than that from pyrolysis. Pyrolysis process resulted in much less oxygen-containing groups on the surface of biochar due to the higher degree of carbonization of biomass compared to the hydrothermal carbonization.

3.3.2. De-mineralization and deashing treatment

Knowledges about the effects of de-mineralization and deashing treatment of biochars on their adsorption of contaminants from water are limited. However, it is noted that these treatments can have significant influence on the adsorption property of biochar. This is mainly because that deashing can greatly influence the composition and the surface characteristics of the biochar. All surface element contents decreased after deashing except for carbon. Zhang et al. (2013b) stated that adsorption increased greatly on the deashed biochar as the removal of inorganic compounds, which blocked some organic adsorption sites in the original biochars. Sun et al. (2013a) studied the impact of deashing treatment on biochar structural properties and adsorption properties of phenanthrene. They reported that biochars possessed more hydrophobic domains and less polar functional groups after deashing. As a result, favorable and hydrophobic adsorption sites of organic matter increased, which could enhance phenanthrene adsorption. Furthermore, they found that this effect was more prominent for biochars produced at high temperature. On the contrary, Xu et al. (2011) reported that rice hull derived biochar exhibited greater removal ability toward methyl violet than water-washed biochar. The removed soluble salts and soluble alkaline materials in the biochar by washing have a positive effect on the adsorption of methyl violet. However, the effect of de-mineralization and deashing treatment is equivocal at present. The experimental evidence of such influence is very scarce, which needs further investigations.

3.3.3. Solution pH

The solution pH is one of the most vital parameters in the optimization of adsorption process. The influence of pH on adsorption was dependent on types of biochars and the target contaminants. It affects not only the adsorbent surface charge, but also the degree of ionization and speciation of the adsorbate (Kołodyńska et al., 2012; Regmi et al., 2012; Li et al., 2013a; Zhang et al., 2013d). Thus most of studies involved in contaminants adsorption onto biochars took the pH effect into account.

Biochar carried various surface functional groups (mainly oxygencontaining groups, e.g. carboxylate, -COOH; and hydroxyl, -OH). The behavior of these functional groups change with the increase of the solution pH. At low pH, most of these functional groups present on biochars are protonated and presented in positively charged form. For pH < pH_{pzc} (point of zero charge), the biochar surface is positively charged, favoring adsorption of the anions (Oh et al., 2012; Abdel-Fattah et al., 2014). In addition, the presence of a large number of H^+ and H_3O^+ in the aqueous solution may compete with the cation for adsorption sites available on biochars. Thus electrostatic repulsion will occur between cation contaminants and positively charged biochars surface thus a lower adsorption was observed at low pH in most of the studies. With the increase of pH value, the competition of metal ions and protons for binding sites decreased and more binding sites are released due to the deprotonation of functional groups (Lu et al., 2012). The surface of biochar is negatively charged when pH > pH_{pzc}. Therefore, in the higher pH range, the cations can be easily captured by biochar surface.

These trends were observed in the studies of different heavy metals adsorption on various biochars. As for the metal cations, most studies reported that the adsorption capacity increased with increasing pH. Chen et al. (2011) used biochars produced by pyrolysis of hardwood and corn straw for adsorption of copper and zinc. They found that the adsorption capacity increased with increasing pH and peaked at pH 5. As the pH values were higher than five, there was a slightly decreasing trend, which might be due to the formation of hydroxide complexes. The results of another study of Cu(II) adsorption on three different biochars indicated that the adsorption of Cu(II) was increased with increasing suspension pH from 3.5 to 6.0 (Tong et al., 2011). Another study observed the similar trend that an increase in pH enhanced Pb adsorption on sludgederived biochar (Lu et al., 2012). On the contrary, the adsorption of negatively charged metal ions such as Cr(VI) was found to behave differently with the decrease of pH (Zhang et al., 2013c; Abdel-Fattah et al., 2014), which was attributed to the strong interaction between the positively charged functional groups of biochar and the negatively charged chromate ions (i.e., CrO_4^{2-} , $Cr_2O_7^{2-}$) at lower pH (Abdel-Fattah et al., 2014). Dong et al. (2011) studied the Cr(VI) adsorption by using sugar beet tailing (SBT) biochar when the pH ranged from 1 to 6, and the results indicated that removal of Cr(VI)

decreased significantly with the increase of pH values and the optimum solution pH for removal of Cr by SBT biochar was 2. The decrease in Cr(VI) removal as pH increased may be attributed to the increase of OH⁻ competition for Cr(VI) species for the adsorption sites on the biochar.

The solution pH also significantly affected the metal speciation, which in turn influence the adsorption of heavy metals by biochar. To assess the variation of metal speciation with respect to different pH, many researchers have used the Visual MINTEQ to calculate the speciation of metals (Kumar et al., 2011; Bernardo et al., 2013). At very high pH values, the adsorption of metal cation is attributed to the formation of metal hydroxide species such as soluble M(OH)⁺ and/or insoluble precipitate of M(OH)₂. In a study of U(VI) adsorption onto biochar, the researchers calculated the speciation of uranium in different pH system. They reported that adsorption of UO_2^{2+} ions was less preferred at low pH due to the positively charged biochar surface (pH < 3.5). An increase in pH resulted in a less positive biochar surface that adsorbed the cationic uranium species $[(UO_2)_2(OH)_2^{2+}, UO_2OH^+, (UO_2)_3(OH)^{5+}].$ Around the neutral pH, U(VI) speciation was dominated by anionic uranyl carbonate $[(UO_2)_2CO_3(OH)^{3-}, UO_2(CO_3)_3^{4-}, UO_2(CO_3)_2^{2-}]$ and hence adsorption onto biochar decreased beyond pH 6.2 (Kumar et al., 2011). At acidic conditions, Pb was present in solution as Pb2+, but the strong positive charge surface of chars restrained the adsorption of lead ion by electrostatic repulsion. As pH increased to neutral, lead still existed mostly as free ion, but the competition effect with H⁺ markedly decreased. At alkaline conditions, lead precipitated as hydroxide (Bernardo et al., 2013).

Further various researchers have studied the effect of pH on organic contaminants and other inorganic contaminants adsorption by biochars. The results showed that the adsorption of these contaminants on biochar was also highly pH-dependent due to the change of biochar surface charge and contaminants properties with the change of solution pH. Parshetti et al. (2014) evaluated the effect of pH (3.0–9.0) on the adsorption of textile dyes by food waste biochar. Their results showed that biochar had high dve adsorption efficiency at alkaline pH due to the electrostatic interaction between the cationic dve molecules and negatively charged surface of biochar. However, the lower adsorption efficiency at acidic pH can be due to the protonation of the dye and the presence of excess H⁺ ions that may compete with the cationic dye molecules for adsorption sites available on biochar. Tsai and Chen (2013) reported that the adsorption capacity of paraguat onto the biochar significantly increased when the pH of aqueous solution changed from 4.5 to 7.5 due to the increasing number of negatively charged sites. Similar trends were also found in the adsorption of methyl violet (Xu et al., 2011) and oxytetracycline (Jia et al., 2013). Oh et al. (2012) investigated the effect of pH on the fluoride adsorption by the water treatment sludge biochar, which can also be explained on the basis of pH_{pzc}.

3.3.4. Co-existed ions

The co-existence of ions exert significant influence on the equilibrium adsorption capacity, especially for the application of biochar in the real water system, because complex pollutants usually co-exist in environment, and have interaction effects on the adsorption efficiency. The studies of adsorption co-existed ions can aid in a better understanding of biochar adsorption mechanism of contaminants in the environment. Jia et al. (2013) investigated the effects of metal ions on the adsorption of oxytetracycline (OTC) by maize straw derived biochar. It turned out that the presence of heavy metals had different effects on OTC adsorption to biochar: insignificant by Cd²⁺, slight facilitation by Zn²⁺, slight inhibition by Pb²⁺, and Cu²⁺ facilitated the adsorption of OTC at all measured pH values. In another study targeting the adsorption ability of the biochar for co-existed atrazine and simazine, the results implied that the adsorption ability of the biochar for two contaminants decreased when they co-existed in the aqueous environment (Zheng et al., 2010). When phenanthrene (PHE) and Hg(II) co-existed in aqueous solution, Kong et al. (2011) observed direct competitive adsorption, each one suppressing another, resulting in decreased adsorption. However, Wang et al. (2013) found that co-existence of humic acid and metal cations increased polychlorinated biphenyls adsorption on the biochars. In any case, the precise mechanism behind these influences still remains equivocal. These apparently contradictory results suggest that further studies focused on analyzing the effects of competitive adsorption and ionic strength of biochars are required.

The polluted water used in the published adsorption studies were all simulation wastewater, which still had gaps with the actual situation. The application of biochar for actual wastewater treatment is still lacked. In addition, the complex pollutants and various ions usually co-exist in the real water system. They may have significant influence on the equilibrium adsorption capacity, which cannot be ignored. In order to make the study consistent with the real situation and have a good understanding of the influence mechanism, the background cations and anions and their concentrations (ionic strength) in solution need to be carefully evaluated on an individual basis.

3.3.5. Dosage of adsorbent

The dosage of adsorbent has significant influence on the adsorption efficiency. Applying an optimum dosage of biochar to contaminants removal is crucial for its cost-effective application. Chen et al. (2011) reported that the increase of the concentration of biochar decreased the adsorption efficiencies. The highest observed metal sorption efficiencies for both hardwood and corn straw derived biochar were at 1 g L^{-1} . While, increasing the adsorbent concentration did result in an increased removal efficiency of the total heavy metals due to the increase in total amount of active sites. Similar results were found by Tsai and Chen (2013). They stated that the number of adsorption sites increased in line with the increase of adsorbent dosage (i.e., $0.10-0.30 \text{ g L}^{-1}$). However, the adsorption efficiency of the swine-manure-derived biochar decreased as its mass increased. In another study, the researchers reported that the removal efficiency of methylene blue dye increased with increasing biochar dose from 2 to 8 g L^{-1} at a constant methylene blue dye concentration, which can be attributed to the increase in available adsorption surface and the availability of more adsorption sites (Sun et al., 2013b).

3.3.6. Temperature

Most previous studies have reported that the adsorption of contaminants by biochars appeared to be an endothermic process and the adsorption capacity increased with increasing temperature (Liu and Zhang, 2009; Chen et al., 2011; Zhang et al., 2013d). Meng et al. (2014) studied the effect of temperature (at 15, 25 and 35 °C) on Cu(II) adsorption onto biochar derived from swine manure, and the thermodynamic parameters were calculated. The positive values of ΔH^0 indicated that the reaction was endothermic. In another study of textile dyes adsorption onto food waste biochar at 20, 30, and 40 °C, the negative values of ΔG^{O} and the positive values of ΔH^0 indicated that adsorption of dyes onto biochar was spontaneous and endothermic. The increase in the absolute values of ΔG^{O} with the increase of temperature suggested that the adsorption of dyes onto biochar was more favorable at higher temperatures (Parshetti et al., 2014). Liu and Zhang (2009) reported that higher temperature favored lead ions adsorption onto pinewood and rice husk derived biochar. The enhanced temperature provided sufficient energy for lead ions to be captured onto the interior structure of biochar. Sun et al. (2013b) investigated the effect of temperature on adsorption capacity for cationic methylene blue dve (MB) onto biochar at 30, 40 and 50 °C. The results demonstrated that the effect of temperature on the adsorption performance of MB was significantly enhanced for eucalyptus biochar with the temperature increasing to 50 °C. This result probably occurred because of the increase in diffusion rate of MB with increasing temperature.

3.4. The management of spent biochar

Since the application of biochar for the removal of pollutants from aqueous solutions is mainly dealing with toxic pollutants, the disposal process of the spent biochar is an important issue to consider. The schematic diagram of the system for pollutants removal from water using biochar, desorption/regeneration of biochars, and other treatment processes are shown in Fig. 3. Specifically, biochar loaded with ammonium, nitrate, and phosphate, and without other toxic pollutants, can be used as a slow-release



Fig. 3. The schematic diagram of the system for pollutants removal from water, desorption/regeneration of biochars, and other treatment processes.

fertilizer to enhance soil fertility (Yao et al., 2011b, 2013b; Zhang et al., 2013a). However, the biochars that were used to adsorb toxic pollutants such as heavy metals and organic pollutants need to be handled with care.

Desorption/regeneration properties were investigated by several studies, which help to determine the reusability of an adsorbent and evaluate the economic feasibility. Zhang et al. (2013d) reported that the adsorbed U(VI) could be desorbed effectively from the spent biochar in four times of adsorption-desorption cycles using 0.05 mol L⁻¹ HCl. In another study, dye-loaded biochar was desorbed using ethanol. The results indicated that the food waste biochar could be used repeatedly without much loss in the total adsorption capacity of the dyes (Parshetti et al., 2014). However, the wide source of waste biomass for biochar production may make the recovery process economically unnecessary. Therefore, the assessment of the economic feasibility of desorption/regeneration process is needed in the future adsorption process. In addition, the regenerated biochars also have their limited usage cycles. The exhausted biochars, which have gone through several times of adsorption-desorption cycles and exhibit low adsorption ability, are also needed to be careful treated due to their potential toxicity.

In order to prevent extra pollution, the treatment of toxic pollutants-loaded biochar and the exhausted biochar must follow standards of hazardous waste treatment. Several methods such as seal up for safekeeping, incineration and safe landfill can be used in the treatment processes. However, little information is available about the disposal of spent biochar using these methods. The stability, potential secondary pollution, effect on the carbon sequestration, and economical feasibility of using these methods to deal with the spent biochar are unclear. Therefore, how to deal with the biochar loaded with various contaminants may become a new challenge to facilitate the biochar's practical application and much more research should be carried out in future.

4. Mechanism of adsorption

For evaluating the removal efficiency of the contaminants by biochars, the identification of the underlying mechanisms of the adsorption process is needed. The adsorption behavior of biochar for different contaminants (i.e., heavy metals, organic pollutants and other pollutants) are different and well correlated with the properties of contaminants. In addition, the adsorption mechanism may also depend on biochar's various properties including surface functional groups, specific surface area, porous structure and mineral components.

4.1. Heavy metals

As for heavy metals, the possible adsorption mechanisms usually involved integrative effects of several kinds of interactions including electrostatic attraction, ion-exchange, physical adsorption, surface complexation and/or precipitation. The various mechanisms proposed for the interaction of biochar with heavy metals are summarized in Fig. 4a. The specific mechanisms of different heavy metals are different and the appropriate properties of biochars make a great contribution to the adsorption of heavy metals.

Abundant surface functional groups (mainly oxygen-containing groups, e.g. carboxylate, —COOH; and hydroxyl, —OH) are existed on biochar's surface, which can have strong interactions with heavy metals such as electrostatic attraction, ion-exchange and surface complexation. These effects can be evidenced by the changes in functional groups of biochar before and after the metal

adsorption (Khare et al., 2013). Dong et al. (2011) hypothesized that sugar beet tailing biochar effectively removed Cr(VI) via electrostatic attraction of Cr(VI) coupled with Cr(VI) reduction to Cr(III) and Cr(III) complexation. They summarized the adsorption process into three parts: first, the negatively charged Cr(VI) species were migrated to the positively charged surfaces of biochar (at low pH) with the help of electrostatic driving forces; Second, Cr(VI) was reduced to Cr(III) by the participation of hydrogen ions and the electron donors from biochar; And finally, part of the Cr(III) reduced from Cr(VI) was released to the aqueous solution, and the other part of Cr(III) was complexed with the function groups on biochar. Lu et al. (2012) also proposed that the functional groups played an important role in Pb adsorption on a sludge derived biochar, which including metal exchange with K⁺ and Na⁺ due to the electrostatic outer-sphere complexation, surface complexation with free carboxyl functional groups and free hydroxvl functional groups, and inner-sphere complexation with free hydroxyl groups. Similar mechanisms can also be seen in the adsorption of Hg(II) onto soybean stalk-based biochar (Kong et al., 2011) and the adsorption of Cd(II) on corn straw biochar (Sun et al., 2014).

In addition, the mineral components in biochar played a crucial role in the adsorption process. Xu et al. (2013b) compared the simultaneously removal effect of Pb, Cu, Zn, and Cd from aqueous solutions by rice husk biochar and dairy manure biochar. The results indicated that the removal ability varied with different biochar feedstock sources and the mineral components such as CO₃²⁻, PO₄³⁻ originated from the feedstock play an important role in the adsorption ability of biochar. In another study of Cu, Zn, and Cd removal by the dairy manure-derived biochar, the researchers found that the biochar produced from dairy manure were rich in PO_4^{3-} and CO_3^{2-} . These mineral components served as additional adsorption sites, contributing to the biochar's high adsorption capacity for heavy metals (Xu et al., 2013c). Similar result was found in the adsorption of Pb by dairy-manure derived biochar. They hypothesized that high Pb removal efficiency by biochar may be attributed to the formation of Pb-phosphate precipitate $Pb_{9}(PO_{4})_{6}$ and the Pb-carbonate precipitation $Pb_{3}(CO_{3})_{2}(OH)_{2}$ (Cao et al., 2009). Qian and Chen (2013) stated that the complexation of Al with organic groups (hydroxyl and carboxyl), the surface adsorption, and co-precipitation of Al with silicate particles (as KAlSi₃O₈) all contributed to Al adsorption onto biochar.

Furthermore, the surface area and porous structure of biochar can also have effects on the adsorption of heavy metals. Biochars have various magnitudes of surface areas and pores within the particles (Table S2), which enable them easily accessible to metals (Khare et al., 2013). However, as the literature data reported, the surface area and porous structure of biochar seem to have less effect on heavy metal adsorption than oxygen-containing functional groups. Ding et al. (2014) reported that the oxygen functional groups were probably responsible for the high Pb sorption onto low temperature biochars (250 and 400 °C) whereas intraparticle diffusion was mainly responsible for low Pb sorption onto high temperature biochars (500 and 600 °C). Samsuri et al. (2014) used oil palm biochar and rice husk biochar to adsorb different heavy metals, the results showed that the former with lower surface area exhibited a higher adsorption capacity for the heavy metals than the latter, suggesting that surface area was less important than oxygen-containing functional groups.

4.2. Organic pollutants

The adsorption mechanisms by which organic contaminants bind to biochars were also combined with different kinds of interactions. In general, electrostatic interaction, hydrophobic effect, hydrogen



Fig. 4. Summary of proposed mechanisms for (a) heavy metals and (b) organic contaminants adsorption on biochars.

bonds, and pore-filling may be the main mechanisms for the adsorption of organic contaminants onto biochar. The various mechanisms proposed for the interaction of biochar with organic contaminants are summarized in Fig. 4b. The specific mechanisms of different organic pollutants are also different and well correlated with the properties of biochars.

Firstly, the surface properties of biochar played a major role in the adsorption of organic pollutants. Surface of biochar is heterogeneous

due to the co-existed carbonized and non-carbonized fractions. and the carbonized and non-carbonized phases of biochar generally represent different adsorption mechanisms. The uptake of organic compound was both decided by partition into the non-carbonized organic matter and by adsorption onto the carbonized matter (Chen et al., 2008; Cao et al., 2009; Zheng et al., 2010). The results of different studies collected suggests that electrostatic attraction was the dominant mechanism for adsorption of organic contaminants onto the chars, with others performed as a contributing adsorption mechanism (Inyang et al., 2014). Qiu et al. (2009) studied the mechanism of dye adsorption on a straw-based biochar. They proposed that the mechanisms of dye adsorption involved π - π interactions between dye molecules and graphene layers of biochar, the electrostatic attraction/repulsion and the intermolecular hydrogen bonding. In the further study, Xu et al. (2011) studied the methyl violet adsorption mechanisms by using zeta potential, FTIR-PAS, adsorption isotherms and CEC. They reported that electrostatic attraction, specific interaction between the dye and the groups of -COO- and phenolic -OH, and surface precipitation were contributed to the adsorption of methyl violet on biochars. Zhang et al. (2013b) stated that the adsorption of carbaryl and atrazine on pig manure-derived biochars could explain by several processes including hydrophobic effect, pore-filling and $\pi - \pi$ electron donor-acceptor interactions. Xie et al. (2014) reported that the adsorption of sulfonamides by different biochars correlate well with the degree of graphitization, indicating that π - π electron-donor-acceptor interaction between the sulfonamides molecules and the graphitic surfaces of the biochars was the predominant adsorption mechanism

In addition, pore-filling was another important mechanism to organic compounds adsorption on biochars (Chen et al., 2012c). The adsorption was in correlation with surface properties of biochars and the adsorption capability is directly proportional to the micropore surface area (Han et al., 2013). Zhu et al. (2014) stated that the high surface areas and pore volumes of carbonaceous material generally promoted organic pollutants adsorption, due to the prominent pore-filling effect. This adsorption mechanism was also reported by Han et al. (2013) and Inyang et al. (2014) related to the studies on the adsorption of phenol and methylene blue by biochars from water.

5. Problems, sustainability, and potential application of biochar

5.1. Potential negative effects

It is noted that biochars have significant removal ability for various contaminants (i.e. heavy metals, organic pollutants, and other inorganic pollutants) from water. However, further use of biochar in environmental management, potential negative effects associated with the use of biochar in aqueous must be considered before expanding use in practice. The potential toxic elements, specifically, heavy metals, metalloids and polycyclic aromatic hydrocarbons (PAHs) inevitably form and associate with biochar. Some researchers have investigated the concentrations of extractable toxic elements contained within the biochar and made some recommendations regarding to minimizing the risk of potential toxic element. Based on the presently reported, most toxic element associated with biochar are likely to be minimal and can thus be acceptable (Freddo et al., 2012; Hale et al., 2012; Agrafioti et al., 2013). Pyrolysis may also inhibit the potential release of heavy metals from the biochars (Zhang et al., 2013c). The yield and composition of toxic element associated with the biochars are strongly dependent upon feedstock material and pyrolytic temperature. Keiluweit et al. (2012) reported that grass biochar contained significantly higher levels of PAHs than wood biochar, and high-temperature biochars appear to be more secure than lowtemperature biochars. Similar results were also found by Hale et al. (2012). Other factors like pyrolysis technology, pyrolysis time and the condition of polluted water all affected the level of toxins in the biochars (Hale et al., 2012; Keiluweit et al., 2012). In this context, the application of biochar in water treatment may not be easily brought into schedule. More and more specific and persuasive researches are needed in the future.

Despite several studies presently reported that most toxic element associated with biochar are likely to be minimal and can thus be acceptable, it is unknown how variations in pyrolytic temperature and feedstock type affect concentration and composition of these toxic elements. And the stability of these toxic elements in a longer period is still equivocal. To close these knowledge gaps, the security of biochars produced with different feedstocks under varying production conditions should be continuously investigated at large time scale.

5.2. Sustainable use of biochar

For a sustainable biochar development and its safe use as a soil amendment, the International Biochar Initiative (IBI) has established standards (*Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil*) to identify certain qualities and characteristics of biochar materials, and report common research requirements for researchers (Initiative, 2012). These standards are updated continually. The further application of biochar in water should imitate this way. Guidelines for biochar that is used in water are also needed.

5.3. Potential application of biochar

Very little information is now available regarding biochar application in the treatment of contaminated sediment. Considering biochar's excellent adsorption ability in water pollutants, it can be used as a new potential in-situ amendments sorbent for contaminated sediment management (Ghosh et al., 2011). Consequently, further research studies should focus on analyzing the feasibility of this assumption, which offers an exciting opportunity for both carbon sequestration and sediment remediation.

6. Conclusions

In the present review, we focused on recent developments related to the removal of heavy metals, organic contaminants and other inorganic contaminants from water using biochar. A survey of the literature on the production of biochars reveals a wide variety of biomass materials have been used as the feedstocks and pyrolyzed by different processes to tackle water pollution. The properties of resultant biochars were profoundly affected by pyrolytic temperature, residence time, feedstock, and pyrolysis technology. The results of characterization analyses and adsorption experiment showed that biochar can be used as a promising adsorbent. An analysis of adsorption mechanisms reveals that different of interactions including electrostatic attraction, kinds ion-exchange, physical adsorption, and chemical bonding (complexation and/or precipitation) are predominantly responsible for binding water pollutants. All researches about the application of biochar in aqueous pointed to the same conclusion that biochar can be a novel and feasible adsorbent. This is not only because of the biochars' excellent adsorption ability, but also their environmental and economic benefits. Despite the use of biochar as adsorbents is increasing, a number of research gaps and uncertainties still exist as identified in this review. To close these knowledge gaps, more relevant investigations are needed in further research.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere. 2014.12.058.

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