Chemosphere 99 (2014) 19–33

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Review

Biochar as a sorbent for contaminant management in soil and water: A review

Mahtab Ahmad[a,b], Anushka Upamali Rajapaksha[a], Jung Eun Lim[a], Ming Zhang[c], Nanthi Bolan[d], Dinesh Mohan[e], Meththika Vithanage[f], Sang Soo Lee[a], Yong Sik Ok[a,c,g,*]

[a] *Korea Biochar Research Center, Kangwon National University, Chuncheon 200-701, Republic of Korea*
[b] *University Institute of Biochemistry and Biotechnology, PMAS Arid Agriculture University, Rawalpindi, Pakistan*
[c] *Department of Environmental Engineering, China Jiliang University, Hangzhou, Zhejiang 310018, PR China*
[d] *Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA, Australia*
[e] *School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India*
[f] *Chemical and Environmental Systems Modeling Research Group, Institute of Fundamental Studies, Kandy, Sri Lanka*
[g] *Department of Renewable Resources, University of Alberta, Alberta, Canada*

HIGHLIGHTS

- This manuscript reviews recent findings published on biochar.
- Physical architecture and composition of biochars are critical for soil and water remediation.
- Sorption capacity depends on surface area, microporosity, and hydrophobicity of biochar.
- Long-term effects of biochar on contaminant stability in soil should be investigated.

ARTICLE INFO

Article history:
Received 23 June 2013
Received in revised form 18 October 2013
Accepted 20 October 2013
Available online 27 November 2013

Keywords:
Black carbon
Charcoal
Activated carbon
Slow pyrolysis
Bioavailability
Amendment

ABSTRACT

Biochar is a stable carbon-rich by-product synthesized through pyrolysis/carbonization of plant- and animal-based biomass. An increasing interest in the beneficial application of biochar has opened up multidisciplinary areas for science and engineering. The potential biochar applications include carbon sequestration, soil fertility improvement, pollution remediation, and agricultural by-product/waste recycling. The key parameters controlling its properties include pyrolysis temperature, residence time, heat transfer rate, and feedstock type. The efficacy of biochar in contaminant management depends on its surface area, pore size distribution and ion-exchange capacity. Physical architecture and molecular composition of biochar could be critical for practical application to soil and water. Relatively high pyrolysis temperatures generally produce biochars that are effective in the sorption of organic contaminants by increasing surface area, microporosity, and hydrophobicity; whereas the biochars obtained at low temperatures are more suitable for removing inorganic/polar organic contaminants by oxygen-containing functional groups, electrostatic attraction, and precipitation. However, due to complexity of soil–water system in nature, the effectiveness of biochars on remediation of various organic/inorganic contaminants is still uncertain. In this review, a succinct overview of current biochar use as a sorbent for contaminant management in soil and water is summarized and discussed.

Contents

---

* Corresponding author at: Korea Biochar Research Center, Kangwon National University, Chuncheon 200-701, Republic of Korea. Tel.: +82 33 250 6443.
E-mail address: soilok@kangwon.ac.kr (Y.S. Ok).

http://dx.doi.org/10.1016/j.chemosphere.2013.10.071

1. Introduction

1.1. Background and biochar definition

The origin of biochar is connected to the ancient Amerindian populations in the Amazon region, locally known as Terra Preta de Indio, where dark earth was created through the use of slash-and-char techniques (Lehmann, 2009; Lehmann and Joseph, 2009). Research on Terra Preta soils (Hortic Anthrosols) in Amazonia has revealed the effects of biochar on functionalization of soils. Especially, because the biochar has been known as an excellent soil amendment for soil fertility and sustainability, many researchers and farmers worldwide are paying attention to its hidden secrets. Biochar is also recognized as a very significant tool of environmental management (Lehmann and Joseph, 2009).

Biochar is a newly constructed scientific term. According to Lehmann and Joseph (2009), it is defined as "*a carbon (C)-rich product when biomass such as wood, manure or leaves is heated in a closed container with little or unavailable air*" (Lehmann and Joseph, 2009). Shackley et al. (2012) defined biochar more descriptively as "*the porous carbonaceous solid produced by the thermochemical conversion of organic materials in an oxygen depleted atmosphere that has physicochemical properties suitable for safe and long-term storage of carbon in the environment*". Verheijen et al. (2010) also defined biochar as "*biomass that has been pyrolyzed in a zero or low oxygen environment applied to soil at a specific site that is expected to sustainably sequester C and concurrently improve soil functions under current and future management, while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health*". The International Biochar Initiative (IBI) standardized its definition as "*a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment*" (IBI, 2012). All of these definitions are directly or indirectly related to the biochar production condition and its application to soil. Lehmann and Joseph (2009) distinguished biochar operationally from charcoal. Primarily, the difference between these two terms lies in the end use. The charcoal is a source of charred organic matter for producing fuel and energy whereas the biochar can be applied for carbon sequestration and environmental management. The term hydrochar is closely related to biochar; however, it is distinguished by different condition like the hydrothermal carbonization of biomass (Libra et al., 2011). In general, biochar is produced by dry carbonization or pyrolysis and gasification of biomass, whereas hydrochar is produced as a slurry in water by hydrothermal carbonization of biomass under pressure. The two chars differ widely in chemical and physical properties (Bargmann et al., 2013).

1.2. Biochar for environmental management

Four major areas where biochar is being used in environmental management include (i) soil improvement, (ii) waste management, (iii) climate change mitigation, and (iv) energy production (Lehmann and Joseph, 2009).

Because of its high organic C content, biochar has the potential to serve as a soil conditioner to improve the physicochemical and biological properties of soils. Soil water retention capacity increases with increase in organic C. About 18% increase in the water holding capacity of soil containing biochar was reported (Glaser et al., 2002). Soil water holding capacity is related to hydrophobicity and surface area of biochar, and the improved soil structure following biochar application (Verheijen et al., 2010). A decrease of nutrient leaching due to biochar application has been also reported (Sohi et al., 2009). Biochar generally has a neutral to alkaline pH; however, acidic biochar has been also reported (Chan et al., 2007). The pH of biochar depends on various factors including feedstock type and the thermochemical process of production. The alkaline pH of biochar induces a liming effect on acidic soils, thereby possibly increasing plant productivity. The extent of liming effect of biochar depends on its acid neutralizing capacity that varies depending on the feedstock and pyrolysis temperature. For example, biochar derived from paper mill waste pyrolyzed at 550 °C had a liming value around 30% that of $CaCO_3$ (Zweiten et al., 2010). Significant increases in seed germination, plant growth, and crop yields have been reported in the soils amended with biochars (Glaser et al., 2002). Applying biochar together with organic or inorganic fertilizers can even enhance crop yields (Lehmann et al., 2002). Increased microbial population and microbial activity in soils amended with biochar have also been observed (Verheijen et al., 2010; Lehmann et al., 2011). Significant changes in soil microbial communities and enzyme activities influence biogeochemical processes in soils (Lehmann et al., 2011; Awad et al., 2012). The effects of biochar on soil fauna have been scarcely studied besides a number of studies on earthworm activity in soil. Weyers and Spokas (2011) reported that the short-term negative effects altered to the long-term null effects on earthworm population in soils amended with biochar. Negative effects of biochar on earthworm population are postulated to be related to rise in soil pH by biochars derived from sludges, manures or crop residue. However, wood-based biochars showed null to positive impacts on earthworm population (Weyers and Spokas, 2011). Recently, Li et al. (2011) recommended that a wet biochar application to soil could help mitigate avoidance of earthworms by preventing desiccation.

One of the major issues with applying biochar is its priming effect on soil native C (Wardle et al., 2008; Awad et al., 2013). Biochar accelerates the decomposition of soil native C (i.e. the positive priming effect) by improving microbial populations (Kuzyakov et al., 2009) and the chemical hydrolysis by increasing soil pH (Yu et al., 2013). On the contrary, others have shown that the biochar increases the adsorption of dissolved organic C (Kwon and Pignatello, 2005; Zimmerman et al., 2011), thereby decreasing its decomposition rate (i.e. the negative priming effect). This negative priming effect has attributed to the toxicity of biochar, thereby resulting in a decrease in microbial activity (Zimmerman et al., 2011). It presumes that physicochemical properties of biochar such as mobile and resident organic matter, and sorption capacity would influence the priming effect of biochar on soil C. Therefore, it is worthwhile to completely characterize biochar before applying in soil.

Biochar has great potential for managing the waste stream originating from animals or plants; thus, decreasing the associated pollution loading to the environment. The use of waste biomass for biochar production is not only economical but also beneficial. The benefits mainly including energy production and climate change mitigation (Barrow, 2012). Waste biomass that has been extensively used to produce biochar includes crop residues, forestry waste, animal manure, food processing waste, paper mill waste, municipal solid waste, and sewage sludge (Brick, 2010; Chen et al., 2011; Cantrell et al., 2012; Enders et al., 2012). Notably, pyrolyzing the waste biomass, particularly animal manure and sewage sludge, kills any microbes present, thereby reducing the environmental health effects (Lehmann and Joseph, 2009). However, the persistence of toxic heavy metals in biochar developed from sewage sludge and municipal solid waste (Lu et al., 2012) must be carefully handled before long-term application to soils.

Converting biomass into biochar and its application to soils have been proposed as one of the best ways to mitigate climate change by sequestering C in soil (Lehmann et al., 2008). The long-term stability of biochar in soil is a key factor affecting a decrease of CO_2 emissions into the atmosphere (Cheng et al., 2008; Kuzyakov et al., 2009; Singh et al., 2012). A recent long-term experiment estimated that the mean residence time of C in biochars varies from 90 to 1600 years depending on the labile and intermediate stable C components (Singh et al., 2012). A few recent studies have shown that biochar can reduce nitrous oxide (N_2O) and methane (CH_4) emissions from soil by both biotic and abiotic mechanisms (Zweiten et al., 2009). Woolf et al. (2010) proposed a sustainable biochar concept by which emissions of greenhouse gases including CH_4 and N_2O can be avoided by pyrolyzing waste biomass. Additionally, the bioenergy produced during the pyrolysis process offsets fossil energy consumption, and half of the C fixed in biomass during photosynthesis is retained (Woolf et al., 2010). Biochar has been estimated to be capable of offsetting a maximum sustainable technical potential (~12%) of current anthropogenic CO_2–C equivalent emissions (Woolf et al., 2010).

Another potential use of converting waste biomass to biochar is the production of bioenergy during the fast and slow pyrolysis processes. This bioenergy can be used as an alternative to fossil energy with low fossil CO_2 emissions (Bolan et al., 2013a). However, bioenergy production is dependent on the pyrolysis conditions, in which the slow pyrolysis results in a lower yield of liquid fuel and more biochar, whereas the fast pyrolysis generates more liquid fuel (bio-oil) with relatively less biochar (Mohan et al., 2006). It is assumed that with an intermediate yield of 35% biochar, a maximum bioenergy output of 8.7 MJ kg^{-1} of biomass could be obtained (Woolf, 2008). However, the production of biochar and/or bioenergy from biomass is still controversial.

Despite the benefits of biochar applications to soil, the mechanisms explaining the interaction between biochar and soil properties have not been fully understood. The long-term effects of biochar applications to different soils should also be monitored (Singh et al., 2012). Both qualitative and quantitative assessments of emissions produced during traditional pyrolysis of waste biomass should be carried out to evaluate their effect on occupational health and safety (Verheijen et al., 2010).

Discharge of environmental contaminants from industrial, residential, and commercial sources degrades the surrounding ecosystems. Soil and water media in an ecosystem are frequently subject to contamination by organic and inorganic contaminants mainly due to anthropogenic activities. Technologies are advancing to remediate contaminated soil and water. One of the most important technologies is to reduce the bioavailability of contaminants, and consequently decrease their accumulation and toxicity in plant and animals. Biochar is emerging as an ameliorant to reduce the bioavailability of contaminants in the environment with additional benefits of soil fertilization and mitigation of climate change (Sohi, 2012).

Environmental remediation has been recognized recently as a promising area where biochar can be successfully applied (Cao et al., 2011; Ahmad et al., 2014). In this review, the effects of pyrolysis conditions, including residence time, feedstock types, temperature and heat transfer rate, on biochar properties, and consequently its efficacy for contaminant remediation are discussed in detail. Special emphasis is given to the mechanistic evidence of the interaction of biochar with soil and water contaminants. Therefore, this review is limited to applying biochar as a green environmental sorbent for the soil and water contaminated with organic/inorganic contaminants.

2. Biochar production and properties

2.1. Biomass pyrolysis

Biomass resources may be limited for the sustainable biochar production. For example, biomass obtained from agricultural crops or plantations as certain types of forests may lead to a decline in soil fertility and an increase in erosion (Cowie et al., 2012). Brick (2010) categorized feedstocks into two groups: (i) primarily produced biomass as a resource of bioenergy and biochar, and (ii) byproducts as waste biomass. Waste biomass has been used extensively for biochar production because of the cost-effectiveness and food security advantages compared to other types of biomass (Brick, 2010).

Biochar can be produced by thermochemical decomposition of biomass at temperatures of 200–900 °C in the presence of little or no oxygen, which is commonly known as pyrolysis (Demirbas and Arin, 2002). Pyrolysis is generally divided into fast, intermediate, and slow depending on the residence time and temperature (Table 1; Mohan et al., 2006). Fast pyrolysis with a very short residence time (<2 s) is often used to produce bio-oil from biomass yielding about 75% bio-oil (Mohan et al., 2006). Slow and intermediate pyrolysis processes with a residence time of few minutes to several hours or even days are generally favored for biochar

Table 1
Pyrolysis processes and products distribution [adopted from Bolan et al. (2013a), Brown (2009), Mohan et al. (2006), and Sohi et al. (2009)].

Process	Temperature (°C)	Residence time	Products		
			Liquid (bio-oil) (%)	Solid (biochar) (%)	Gas (syngas) (%)
Fast pyrolysis	300–1000	Short (<2 s)	75	12	13
Intermediate pyrolysis	~500	Moderate (10–20 s)	50	25	25
Slow pyrolysis	100–1000	Long (5–30 min)	30	35	35
Gasification	>800	Moderate (10–20 s)	5	10	85

Table 2
Characteristics of biochars produced from different feedstocks.

Feedstock	Pyrolysis temperature (°C)	Heating rate (°C min^{-1})	Yield (%)	Mobile matter (%)	Fixed matter (%)	Ash (%)	pH	C (%)	H (%)	O (%)	N (%)	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	References
Broiler litter	350	–	–	–	–	–	–	45.60	4.00	18.30	4.50	60.0	0.000	Uchimiya et al. (2010)
Broiler litter	700	–	–	–	–	–	–	46.00	1.42	7.40	2.82	94.0	0.018	Uchimiya et al. (2010)
Buffalo weed	300	7.0	50.0	44.2	30.4	20.4	8.7	78.09	4.26	7.44	10.21	4.0	0.010	Unpublished data
Buffalo weed	700	7.0	29.0	20.9	46.8	32.3	12.3	84.96	1.09	6.56	7.40	9.3	0.020	Unpublished data
Canola straw	400	20.0	27.4	–	–	–	–	45.70	–	–	0.19	–	–	Tong et al. (2011)
Chicken litter	620	13.0	43–49	16.0	30.8	53.2	–	41.50	1.20	0.70	2.77	–	–	Ro et al. (2010)
Corn cobs	500	–	18.9	–	–	13.3	7.8	77.60	3.05	5.11	0.85	0.0	–	Mullen et al. (2010)
Corn stover	450	–	15.0	12.7	28.7	58.0	–	33.20	1.40	8.60	0.81	12.0	–	Lee et al. (2010)
Corn stover	500	–	17.0	–	–	32.8	7.2	57.29	2.86	5.45	1.47	3.1	–	Mullen et al. (2010)
Cottonseed hull	200	–	83.4	69.3	22.3	3.1	–	51.90	6.00	40.50	0.60	–	–	Uchimiya et al. (2011a)
Cottonseed hull	350	–	36.8	34.9	52.6	5.7	–	77.00	4.53	15.70	1.90	4.7	–	Uchimiya et al. (2011a)
Cottonseed hull	500	–	28.9	18.6	67.0	7.9	–	87.50	2.82	7.60	1.50	0.0	–	Uchimiya et al. (2011a)
Cottonseed hull	650	–	25.4	13.3	70.3	8.3	–	91.00	1.26	5.90	1.60	34.0	–	Uchimiya et al. (2011a)
Cottonseed hull	800	–	24.2	11.4	69.5	9.2	–	90.00	0.60	7.00	1.90	322.0	–	Uchimiya et al. (2011a)
Feed lot	350	2.5	51.1	47.9	23.5	28.7	9.1	53.32	4.05	15.70	3.64	1.3	–	Cantrell et al. (2012)
Feed lot	700	8.3	32.2	19.8	36.3	44.0	10.3	52.41	0.91	7.20	1.70	145.2	–	Cantrell et al. (2012)
Fescue straw	100	–	99.9	69.6	23.5	6.9	–	48.60	7.25	44.10	0.64	1.8	–	Keiluweit et al. (2010)
Fescue straw	200	–	96.9	70.7	23.6	5.7	–	47.20	7.11	45.10	0.61	3.3	–	Keiluweit et al. (2010)
Fescue straw	300	–	75.8	54.4	36.2	9.4	–	59.70	6.64	32.70	1.02	4.5	–	Keiluweit et al. (2010)
Fescue straw	400	–	37.2	26.8	56.9	16.3	–	77.30	4.70	16.70	1.24	8.7	–	Keiluweit et al. (2010)
Fescue straw	500	–	31.4	20.3	64.3	15.4	–	82.20	3.32	13.40	1.09	50.0	–	Keiluweit et al. (2010)
Fescue straw	600	–	29.8	13.5	67.6	18.9	–	89.00	2.47	7.60	0.99	75.0	–	Keiluweit et al. (2010)
Fescue straw	700	–	28.8	9.1	71.6	19.3	–	94.20	1.53	3.60	0.70	139.0	–	Keiluweit et al. (2010)
Oak bark	450	–	–	22.8	64.5	11.1	–	71.25	2.63	12.99	0.46	1.9	1.060	Mohan et al. (2011)
Oak wood	400–450	–	–	15.6	78.3	2.9	–	82.83	2.70	8.05	0.31	2.7	0.410	Mohan et al. (2011)
Orange peel	150	–	82.4	–	–	0.5	–	50.60	6.20	41.00	1.75	22.8	0.023	Chen and Chen (2009)
Orange peel	200	–	61.6	–	–	0.3	–	57.90	5.53	34.40	1.88	7.8	0.010	Chen and Chen (2009)
Orange peel	250	–	48.3	–	–	1.1	–	65.10	5.12	26.50	2.22	33.3	0.020	Chen and Chen (2009)
Orange peel	300	–	37.2	–	–	1.6	–	69.30	4.51	22.20	2.36	32.3	0.031	Chen and Chen (2009)
Orange peel	350	–	33.0	–	–	2.0	–	73.20	4.19	18.30	2.30	51.0	0.010	Chen and Chen (2009)
Orange peel	400	–	30.0	–	–	2.1	–	71.70	3.48	20.80	1.92	34.0	0.010	Chen and Chen (2009)
Orange peel	500	–	26.9	–	–	4.3	–	71.40	2.25	20.30	1.83	42.4	0.019	Chen and Chen (2009)
Orange peel	600	–	26.7	–	–	4.1	–	77.80	1.97	14.40	1.80	7.8	0.008	Chen and Chen (2009)
Orange peel	700	–	22.2			2.8	–	71.60	1.76	22.20	1.72	201.0	0.035	Chen and Chen (2009)
Paper sludge	105	7.0	–	49.3	17.0	31.5	7.9	45.93	5.67	46.80	1.51	4.2	0.020	Unpublished data
Paper sludge	300	7.0	65.8	16.6	30.4	51.2	7.8	60.00	3.71	33.81	2.49	4.3	0.020	Unpublished data

Table 2 (*continued*)

Feedstock	Pyrolysis temperature (°C)	Heating rate (°C min^{-1})	Yield (%)	Mobile matter (%)	Fixed matter (%)	Ash (%)	pH	C (%)	H (%)	O (%)	N (%)	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	References
Paper sludge	700	7.0	40.3	3.2	21.7	73.8	9.9	59.88	0.71	37.89	1.46	145.6	0.070	Unpublished data
Peanut shell	300	7.0	36.9	60.5	37.0	1.2	7.8	68.27	3.85	25.89	1.91	3.1	–	Ahmad et al. (2012a)
Peanut shell	700	7.0	21.9	32.7	58.1	8.9	10.6	83.76	1.75	13.34	1.14	448.2	0.200	Ahmad et al. (2012a)
Peanut straw	400	20.0	28.2	–	–	–	–	42.90	–	–	1.50	–	–	Tong et al. (2011)
Pine needles	100	–	91.2	–	–	1.1	–	50.87	6.15	42.27	0.71	0.7	–	Chen et al. (2008)
Pine needles	200	–	75.3	–	–	0.9	–	57.10	5.71	36.31	0.88	6.2	–	Chen et al. (2008)
Pine needles	250	–	56.1	–	–	1.2	–	61.24	5.54	32.36	0.86	9.5	–	Chen et al. (2008)
Pine needles	300	–	48.6	–	–	1.9	–	68.87	4.31	25.74	1.08	19.9	–	Chen et al. (2008)
Pine needles	400	–	30.0	–	–	2.3	–	77.85	2.95	18.04	1.16	112.4	0.044	Chen et al. (2008)
Pine needles	500	–	26.1	–	–	2.8	–	81.67	2.26	14.96	1.11	236.4	0.095	Chen et al. (2008)
Pine needles	600	–	20.4	–	–	2.8	–	85.36	1.85	11.81	0.98	206.7	0.076	Chen et al. (2008)
Pine needles	700	–	14.0	–	–	2.2	–	86.51	1.28	11.08	1.13	490.8	0.186	Chen et al. (2008)
Pine needles	300	7.0	57.6	38.6	54.2	7.2	6.4	84.19	4.37	7.57	3.88	4.1	–	Unpublished data
Pine needles	500	7.0	31.8	15.8	72.4	11.8	8.1	90.10	2.06	3.74	4.10	13.1	0.015	Unpublished data
Pine needles	700	7.0	25.0	6.2	75.0	18.7	10.6	93.67	0.62	2.07	3.64	390.5	0.120	Unpublished data
Pine shaving	100	–	99.8	77.1	21.7	1.2	–	50.60	6.68	42.70	0.05	1.6	–	Keiluweit et al. (2010)
Pine shaving	200	–	95.9	77.1	21.4	1.5	–	50.90	6.95	42.20	0.04	2.3	–	Keiluweit et al. (2010)
Pine shaving	300	–	62.2	70.3	28.2	1.5	–	54.80	6.50	38.70	0.05	3.0	–	Keiluweit et al. (2010)
Pine shaving	400	–	35.3	36.4	62.2	1.1	–	74.10	4.95	20.90	0.06	28.7	–	Keiluweit et al. (2010)
Pine shaving	500	–	28.4	25.2	72.7	1.4	–	81.90	3.54	14.50	0.08	196.0	–	Keiluweit et al. (2010)
Pine shaving	600	–	23.9	11.1	85.2	3.7	–	89.00	2.99	8.00	0.06	392.0	–	Keiluweit et al. (2010)
Pine shaving	700	–	22.0	6.3	92.0	1.7	–	92.30	1.62	6.00	0.08	347.0	–	Keiluweit et al. (2010)
Pinewood	700	10.0	–	3.2	57.1	38.8	6.6	95.30	0.82	3.76	0.12	29.0	0.130	Liu et al. (2010)
Poplar wood	400	8.0	32.0	–	–	3.5	9.0	67.30	4.42	–	0.78	3.0	–	Kloss et al. (2012)
Poplar wood	460	8.0	–	–	–	5.7	9.2	70.00	3.51	–	0.95	8.2	–	Kloss et al. (2012)
Poplar wood	525	8.0	–	–	–	6.8	8.7	77.90	2.66	–	1.07	55.7	–	Kloss et al. (2012)
Poultry litter	350	2.5	54.3	42.3	27.0	30.7	8.7	51.07	3.79	15.63	4.45	3.9	–	Cantrell et al. (2012)
Poultry litter	700	8.3	36.7	18.3	35.5	46.2	10.3	45.91	1.98	10.53	2.07	50.9	–	Cantrell et al. (2012)
Poultry manure	300	7.0	65.7	19.0	56.5	24.0	8.8	52.90	3.92	34.73	7.80	4.3	0.012	Unpublished data
Poultry manure	400	7.0	54.0	8.2	63.8	28.0	10.6	51.04	3.15	39.35	5.41	11.6	0.027	Unpublished data
Poultry manure	500	7.0	72.0	7.3	68.6	24.0	11.0	51.56	1.87	40.32	5.50	5.8	0.022	Unpublished data
Poultry manure	600	7.0	47.0	5.4	71.6	22.6	11.5	52.28	1.44	40.27	4.24	3.7	0.019	Unpublished data
Poultry manure	700	7.0	47.0	4.1	69.6	24.2	10.7	56.09	1.52	37.19	4.16	6.6	0.020	Unpublished data
Rapeseed plant	400	5.0	39.4	27.1	60.7	12.2	–	71.34	3.93	10.84	1.43	16.0	1.244	Karaosmanoğlu et al. (2000)
Rapeseed plant	500	5.0	35.6	17.5	69.6	12.9	–	75.03	2.62	7.79	1.41	15.7	1.150	Karaosmanoğlu et al. (2000)
Rapeseed plant	600	5.0	32.2	11.5	74.7	13.9	–	78.48	1.88	3.94	1.53	17.6	1.263	Karaosmanoğlu et al. (2000)
Rapeseed plant	700	5.0	29.6	9.0	76.7	14.4	–	79.48	1.20	3.29	1.35	19.3	1.254	Karaosmanoğlu et al. (2000)

(*continued on next page*)

Table 2 (*continued*)

Feedstock	Pyrolysis temperature (°C)	Heating rate (°C min^{-1})	Yield (%)	Mobile matter (%)	Fixed matter (%)	Ash (%)	pH	C (%)	H (%)	O (%)	N (%)	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	References
Rapeseed plant	800	5.0	28.2	6.0	79.7	15.3	–	79.51	0.72	2.61	1.45	19.0	1.155	Karaosmanoğlu et al. (2000)
Rapeseed plant	900	5.0	27.9	16.1	3.6	–	–	79.86	0.42	1.67	1.57	140.4	1.323	Karaosmanoğlu et al. (2000)
Rice husk	500	–	–	–	–	42.2	–	42.10	2.20	12.10	0.50	34.4	0.028	Liu et al. (2012)
Saw dust	450	–	–	40.1	57.2	1.1	5.9	72.00	3.50	24.41	0.08	–	–	Lin et al. (2012)
Saw dust	550	–	–	13.6	82.6	2.8	12.1	85.00	1.00	13.68	0.30	–	–	Lin et al. (2012)
Sewage sludge	300	7.0	70.1	19.8	22.5	56.6	6.8	30.72	3.11	11.16	4.11	4.5	0.010	Unpublished data
Sewage sludge	400	7.0	57.4	8.8	23.5	67.1	6.6	26.62	1.93	10.67	4.07	14.1	0.020	Unpublished data
Sewage sludge	500	7.0	53.8	7.5	20.0	71.9	7.3	20.19	1.08	9.81	2.84	26.2	0.040	Unpublished data
Sewage sludge	600	7.0	51.2	5.8	19.1	74.6	8.3	24.76	0.83	8.41	2.78	35.8	0.040	Unpublished data
Sewage sludge	700	7.0	50.3	4.1	16.6	76.6	8.1	22.04	0.57	7.09	1.73	54.8	0.050	Unpublished data
Soybean stover	300	7.0	37.0	46.3	38.8	10.4	7.3	68.81	4.29	24.99	1.88	5.6	–	Ahmad et al. (2012a)
Soybean stover	700	7.0	21.6	14.7	67.7	17.2	11.3	81.98	1.27	15.45	1.30	420.3	0.190	Ahmad et al. (2012a)
Soybean straw	400	20.0	24.7	–	–	–	–	44.10	–	–	2.38	–	–	Tong et al. (2011)
Spruce wood	400	8.0	36.0	–	–	1.9	6.9	63.50	5.48	–	1.02	1.8	–	Kloss et al. (2012)
Spruce wood	460	8.0	–	–	–	3.0	8.7	79.60	3.32	–	1.24	14.2	–	Kloss et al. (2012)
Spruce wood	525	8.0	–	–	–	4.7	8.6	78.30	3.04	–	1.17	40.4	–	Kloss et al. (2012)
Swine solid	350	2.5	62.3	49.8	17.7	32.5	8.4	51.51	4.91	11.10	3.54	0.9	–	Cantrell et al. (2012)
Swine solid	700	8.3	36.4	13.4	33.8	52.9	9.5	44.06	0.74	4.03	2.61	4.1	–	Cantrell et al. (2012)
Swine solid	620	13.0	43–49	14.1	41.2	44.7	–	50.70	1.90	<0.01	3.26	–	–	Ro et al. (2010)
Tire rubber	200	10.0	93.5	–	–	15.0	–	74.70	6.38	3.92	–	–	–	Lian et al. (2011)
Tire rubber	400	10.0	59.3	–	–	15.4	–	77.70	3.56	3.34	–	24.2	0.080	Lian et al. (2011)
Tire rubber	600	10.0	54.5	–	–	15.6	–	81.30	1.67	1.43	–	51.5	0.120	Lian et al. (2011)
Tire rubber	800	10.0	43.0	–	–	10.5	–	86.00	0.87	2.16	0.47	50.0	0.110	Lian et al. (2011)
Turkey litter	350	2.5	58.1	42.1	23.1	34.8	8.0	49.28	3.60	15.40	4.07	2.6	–	Cantrell et al. (2012)
Turkey litter	700	8.3	39.9	20.8	29.2	49.9	9.9	44.77	0.91	5.80	1.94	66.7	–	Cantrell et al. (2012)
Wheat straw	400	8.0	34.0	–	–	9.7	9.1	65.70	4.05	–	1.05	4.8	–	Kloss et al. (2012)
Wheat straw	460	8.0	–	–	–	12.0	8.7	72.40	3.15	–	1.07	2.8	–	Kloss et al. (2012)
Wheat straw	525	8.0	–	–	–	12.7	9.2	74.40	2.83	–	1.04	14.2	–	Kloss et al. (2012)
Minimum	100	2.5	14.0	3.2	3.6	0.3	5.9	20.19	0.42	0.01	0.04	0.0	0.000	
Maximum	900	20.0	99.9	77.1	92.0	76.6	12.3	95.30	7.25	46.80	10.21	490.8	1.323	
Median	460	7.0	37.0	18.3	52.6	11.1	8.7	69.30	2.97	13.34	1.47	15.0	0.035	
Mean	470	7.9	44.4	25.9	48.0	18.2	8.9	65.48	3.11	17.27	1.92	62.6	0.231	
Mode	700	7.0	46.0	19.8	23.5	1.1	8.7	89.00	1.20	18.30	0.08	0.0	0.020	

production (25–35%) (Brown, 2009). Gasification is different with general pyrolysis process. For gasification, the biomass is converting into gases rich in carbon monoxide and hydrogen by reacting the biomass at high temperature (>700 °C) in a controlled oxygen environment and/or steam. The resulting gas mixture is known as synthetic gas or syngas (Mohan et al., 2006).

2.2. Factors affecting biochar properties

Table 2 summarizes the important key parameters collected from recently published studies on biochar production and their characteristics. A number of feedstocks including crop residues, wood biomass, animal litter, and solid waste have been utilized to produce biochar via slow to intermediate pyrolysis processes. The pyrolysis temperature in these studies varied from 100 to 900 °C with heating rates ranging from 2.5 to 20 °C min^{-1}. Biochar yield was dependent on the feedstock type, pyrolysis temperature, and heating rate. Generally, animal litter and solid waste generated a high yield of biochar compared to that from crop residues and wood biomasses (Enders et al., 2012). The high yield is related to the higher inorganic constituents of the feedstock materials, as indicated by their relatively high ash content. Cantrell et al. (2012) suggested that various inherent metals in animal litter may protect against the loss of volatile material by changing the bond dissociation energies of organic and inorganic C bonds. This finding was supported by Raveendran et al. (1995) who reported a high biochar yield from rice husk, groundnut shells, coir pith, and wheat straw due to the higher levels of K and Zn. Generally, biomass with high lignin content results in high biochar yields (Sohi et al., 2010). Heating rate was the least effective factor in determining biochar yield. Karaosmanoğlu et al. (2000) reported a slight decrease in biochar yield with an increase of the heating rate from 5 to 15 °C min^{-1}.

Pyrolysis temperature plays a significant role in changing biochar characteristics. Uchimiya et al. (2011a) converted cottonseed hulls into biochar at various pyrolysis temperatures ranging from 200 to 800 °C. A rapid decrease in biochar yield was observed at $\leqslant$400 °C due to the loss of volatile matter and non-condensable gases (CO_2, CO, H_2, and CH_4), whereas at >400 °C, a steady biochar yield was observed. The biochar yield at >400 °C was fairly consistent because of the low lignin content in cottonseed hulls. A comprehensive comparison was made by Keiluweit et al. (2010) among different biochars derived from grass and wood biomass based on pyrolysis temperature. A rapid decline in biochar yield at <300 °C was reported due to initial dehydration reactions. Relatively lower lignin contents in grass compared to wood caused an earlier thermal breakdown at low pyrolysis temperatures (200–400 °C). The authors demonstrated by X-ray diffraction (XRD) analysis that turbostratic crystallites appeared in biochars derived from grass and wood at >400 °C. At the same temperature, a pronounced increase in aromatic C and the appearance of condensation reactions were evidenced by the near edge X-ray absorption fine structure spectra of the biochars (Keiluweit et al., 2010). Elemental compositions and their calculated molar ratios have been extensively used in conjunction with Fourier transform infrared spectroscopy to reveal the pyrolysis temperature effects on the functional chemistry of biochars. A rise in pyrolysis temperature increased C content, whereas H and O contents decreased (Table 2). At $\geqslant$700 °C, ~90% C is produced in biochars from different feedstocks (Chen et al., 2008; Keiluweit et al., 2010; Lian et al., 2011; Uchimiya et al., 2011a), which is attributed to the graphitization of C into well-organized layers. Decreased H and O contents with an increase in pyrolysis temperature also results in lower molar H/C and O/C ratios, thereby indicating dehydration and deoxygenation of the biomass. A van Krevelen diagram (Fig. 1), constructed for various biochars clearly demonstrates that a plant-based biomass undergoes dehydration and depolymerization into smaller dissociation products of lignin and cellulose with an increase in pyrolysis temperature (Keiluweit et al., 2010). However, poultry manure- and sewage sludge-derived biochars do not undergo depolymerization because of the absence of lignocellulosic compounds. Chen et al. (2008) showed the decreasing H/C and O/C ratios related to a higher aromaticity and lower polarity of biochars derived from pine needles. These findings were further supported by Chen and Chen (2009) and Uchimiya et al. (2010). Generally, no significant effect of pyrolysis temperature on N contents of biochars derived from various feedstock was observed (Table 2). However, N contents in biochar depend on the type of feedstock. Manure and sewage sludge based biochars are generally N enriched. Relative to other elements, little information is available on S and P contents of biochar that can further add complexity to S and P cycles in soil. Petit et al. (2010) reported that in addition to O-containing groups, S-containing functional groups enhance ammonia retention on char by forming ammonium sulfate salts. Therefore, the role of functional groups in biochar should be addressed for better understanding of biochar effects on nutrient cycling in soil.

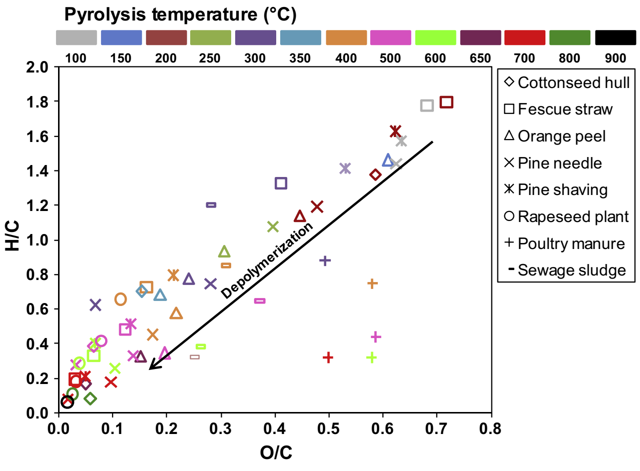

Fig. 1. van Krevelen diagram for various biochars derived from various feedstocks under different pyrolysis temperatures (data taken from Table 2).

Morphology and surface structural changes in biochar are also influenced by pyrolysis temperature (Liu et al., 2010; Uchimiya et al., 2011a). In general, surface area increases with an increase in pyrolysis temperature. However, a reduction in surface area at $\geqslant$700 °C has also been reported (Uchimiya et al., 2011a). Destruction of aliphatic alkyl and ester groups, and exposure of the aromatic lignin core through higher pyrolysis temperatures may be responsible for an increase in surface area (Chen and Chen, 2009). A positive correlation between micropore volume and surface area suggests that the pore size distribution is a key factor responsible for the increase in surface area in biochar (Downie et al., 2009). Biochars produced from animal litter and solid waste feedstocks exhibit lower surface areas compared to biochars produced from crop residue and wood biomass, even at higher pyrolysis temperatures (Table 2). This may be due to the low C content and high molar H/C and O/C ratios in the latter biomass samples, leading to the formation of extensive cross-linkages (Bourke et al., 2007). Notably, the biochars produced at $\geqslant$700 °C and a low heating rate may possess a lower surface area. This lowering in surface area may be due to the development of deformation, cracking or blockage of micropores in biochars (Liu et al., 2010; Lian et al., 2011).

3. Biochar as a universal sorbent

Carbonaceous materials have been used for a long time as sorbents for organic and inorganic contaminants in soil and water (Saeed et al., 2005; Salih et al., 2011; Yang et al., 2011; Ahmad et al., 2012c). Currently, the activated carbon, which is charcoal that has been treated (i.e., activated) with oxygen (in general) to increase microporosity and surface area, is the most commonly used carbonaceous sorbent. The term "activated" is commonly used to describe the enhanced surface area of charcoal upon thermal or chemical treatment. Biochar is quite similar to activated carbon with respect to mutual production via pyrolysis, with medium to high surface areas (Cao et al., 2011). However, unlike activated carbon, biochar is generally not activated or treated (Cao and Harris, 2010; Ahmad et al., 2012a). Additionally, the biochar contains a non-carbonized fraction that may interact with soil contaminants. Specifically, the extent of O-containing carboxyl, hydroxyl, and phenolic surface functional groups in biochar could effectively bind soil contaminants (Uchimiya et al., 2011b). These multi-functional characteristics of biochar show the potential as a very effective environmental sorbent for organic and inorganic contaminants in soil and water. As discussed earlier, the specific biochar properties are mainly affected by pyrolysis temperature, residence time, and feedstock type, which strongly influence biochar sorption properties towards various contaminants; therefore, the selection of proper biochars producing at different conditions should be critical.

Table 3
Biochar utilization for organic contaminants remediation in soil and water.

Contaminant	Biochar type	Matrix	Effect	References
Agro chemicals				
Atrazine	Dairy manure (450 °C)	Soil	Sorption	Cao et al. (2011)
Atrazine	Dairy manure (200 °C)	Water	Partitioning into organic C/sorption	Cao and Harris (2010)
Atrazine and simazine	Green waste (450 °C)	Water	Adsorption and partition	Zheng et al. (2010)
Chloropyrifos and carbofuran	Woodchips (450 and 850 °C)	Soil	Adsorption due to high surface area and nano-porosity	Yu et al. (2009)
Chlorpyrifos and fipronil	Cotton straw (450 and 850 °C)	Water	Adsorption due to high surface area and microporosity	Yang et al. (2010)
Deisopropylatrazine	Broiler litter (350 and 700 °C)	Water	Sorption due to high surface area and aromaticity; sorption on non-carbonized fraction	Uchimiya et al. (2010)
Pentachlorophenol	Bamboo (600 °C)	Soil	Reduced leaching due to diffusion and partition	Xu et al. (2012)
Pentachlorophenol	Rice straw	Soil	Adsorption due to high surface area and microporosity	Lou et al. (2011)
Pyrimethanil	Red gum woodchips (450 and 850 °C)	Water	Adsorption due to high surface area and microporosity	Yu et al. (2010)
Simazine	Hardwood (450 and 600 °C)	Soil	Sorption due to abundance of micropores	Jones et al. (2011)
Norflurazon and fluridone	Grass and wood (200–600 °C)	Water	Sorption on amorphous C phase	Sun et al. (2011)
Antibiotics				
Sulfamethazine	Hardwood (600 °C)	Water	Adsorption due to π–π electron donor–acceptor interaction; negative charge assisted H-bonding	Teixidó et al. (2011)
Sulphamethoxazole	Bamboo (450 and 600 °C) Pepperwood (450 and 600 °C) Sugarcane bagasse (450 and 600 °C) Hickory wood (450 and 600 °C)	Water	Sorption	Yao et al. (2012)
Tylosin	Pulpgrade hardwood and softwood chips (850 and 900 °C)	Soil	Sorption	Jeong et al. (2012)
Tetracycline	Rice husk (450–500 °C)	Water	Formation of π–π interactions between ring structure of tetracycline molecule and graphite-like sheets of biochars	Liu et al. (2012)
Other hydrocarbons				
Brilliant blue and rhodanine dyes	Rice and wheat straw	Water	Electrostatic attraction/repulsion and intermolecular hydrogen bonding	Qiu et al. (2009)
Catechol and humic acid	Hard wood, softwood and grass (250, 400 and 650 °C)	Water	Adsorption due to presence of nano-pores	Kasozi et al. (2010)
m-Dinitrobenzene	Pine needles (100–700 °C)	Water	Transitional adsorption and partition	Chen et al. (2008)
Methyl violet	Crop residue (350 °C)	Water	Electrostatic attraction; interaction between dye and carboxylate and phenolic hydroxyl groups; surface precipitation	Xu et al. (2011)
Naphthalene	Pine needles (100–700 °C)	Water	Transitional adsorption and partition	Chen et al. (2008)
Naphthalene	Orange peel (250, 400 and 700 °C)	Water	Adsorption and partition	Chen et al. (2011a)
Naphthalene and 1-naphthol	Orange peel (150–700 °C)	Water	Adsorption and partition	Chen and Chen (2009)
Nitrobenzene	Pine needles (100–700 °C)	Water	Transitional adsorption and partition	Chen et al. (2008)
Phenanthrene	Pine wood (350 and 700 °C)	Soil	Entrapment in micro- or meso-pores	Zhang et al. (2010)
Phenanthrene	Soybean stalk (300–700 °C)	Water	Partitioning	Kong et al. (2011)
p-Nitrotoluene	Orange peel (250, 400 and 700 °C)	Water	Adsorption and partition	Chen et al. (2011a)
Polycyclic aromatic hydrocarbons (PAHs)	Hard wood	Soil	Sorption and biodegradation	Beesley et al. (2010)
Polycyclic aromatic hydrocarbons (PAHs)	Sewage sludge (500 °C)	Soil	Partitioning	Khan et al. (2013a)
Pyrene	Corn stover (600 °C)	Water	Adsorption due to nano-porosity	Hale et al. (2011)
Pyrene	Saw dust (400 and 700 °C)	Water	Sorption	Zhang et al. (2011)
Trichloroethylene	Soybean stover (300 and 700 °C) Peanut shell (300 and 700 °C)	Water	Sorption	Ahmad et al. (2012a)

3.1. Remediation of organic contaminants in soil and water

The biochar characteristics similar to activated carbon have attracted researchers for use in the organic contaminant removal in water treatment and soil remediation (Zhang et al., 2013). Table 3 summarizes recent studies on biochar applications for the remediation of organically contaminated soil and water. A greater proportion of these studies focused on remediation of aqueous organic

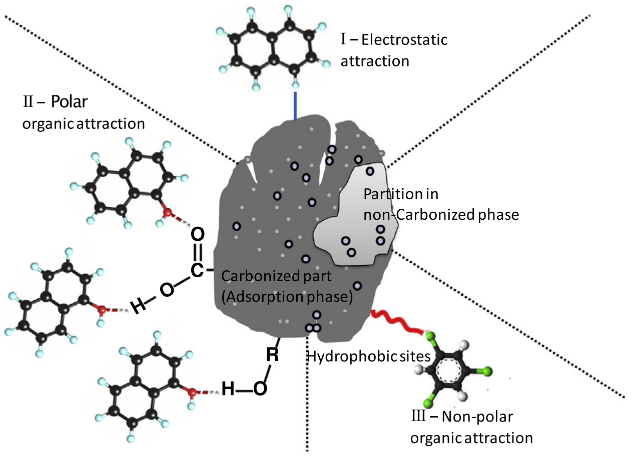

Fig. 2. Postulated mechanisms of the interactions of biochar with organic contaminants. Circles on biochar particle show partition or adsorption. I – electrostatic interaction between biochar and organic contaminant, II – electrostatic attraction between biochar and polar organic contaminant, and III – electrostatic attraction between biochar and non-polar organic contaminant.

contaminants, whereas only a few studies are applicable to soil (Table 3). The greatest concern of organic contaminants has been focused on pesticides, herbicides, polycyclic aromatic hydrocarbons, dyes, and antibiotics (Qiu et al., 2009; Beesley et al., 2010; Zheng et al., 2010; Teixidó et al., 2011; Xu et al., 2012). The various mechanisms proposed for the interaction of biochar with organic contaminants are summarized in Fig. 2. Partitioning or adsorption and electrostatic interactions between organic contaminants and biochar are critical for remediation applications and are discussed in detail in the following sections.

3.1.1. Contaminated water

Sorption of organic contaminants from water onto biochar occurs due to its high surface area and microporosity (Yu et al., 2009; Yang et al., 2010; Lou et al., 2011). Biochars produced at >400 °C are more effective for organic contaminant sorption because of their high surface area and micropore development (Uchimiya et al., 2010; Yang et al., 2010; Ahmad et al., 2012a). Chen et al. (2008) predicted that the partitioning of organic contaminants into non-carbonized biochar fractions derived from pine needles was the major sorption mechanism at low pyrolysis temperatures (100–300 °C), whereas adsorption onto porous carbonized fractions was dominant at high temperatures (400–700 °C). Surface polarity and aromaticity are important characteristics of biochars, as they affect aqueous organic contaminant sorption (Chen et al., 2008). In general, at >500 °C, biochar surfaces become less polar and more aromatic due to the loss of O- and H-containing functional groups, which may further affect organic contaminant adsorption. Uchimiya et al. (2010) reported an increase in the sorption capacity of deisopropylatrazine with an increase in aromaticity of biochar derived from broiler litter at 700 °C. Similar observations were made for trichloroethylene sorption on biochars produced from soybean stover and peanut shells at 700 °C versus at 300 °C (Ahmad et al., 2012a). This was explained with the high aromaticity and low polarity of the biochars produced at 700 °C. In contrast, Sun et al. (2011) reported that the biochars produced at 400 °C with high polarities were more effective on the sorption of norflurazon and fluridone. These different findings are attributed to differences in the nature of the organic compounds. Polar compounds, such as norflurazon and fluridone, are adsorbed by H-bonding between the compounds and the O-containing moieties of the biochars (Sun et al., 2011), whereas non-polar compounds, such as trichloroethylene, access hydrophobic sites on biochar surfaces in the absence of H-bonding between water and O-containing functional groups (Ahmad et al., 2012a). Therefore, the functionality of the target organic contaminant critically affects biochar adsorption capacity. A higher adsorption capacity for 1-naphthol than naphthalene on biochars produced from orange peel at 200–350 °C was reported due to polar-specific interactions between hydroxyl groups in 1-naphthol and polar surfaces of the biochars (Chen and Chen, 2009).

Electrostatic attraction/repulsion between organic contaminants and biochar is another possible adsorption mechanism. Biochar surfaces are normally, negatively charged, which could facilitate the electrostatic attraction of positively charged cationic organic compounds. This electrostatic attraction was reported by Xu et al. (2011) and Qiu et al. (2009) related to the studies on the adsorption of cationic dyes including methyl violet and rhodanine from water. Aromatic π-systems in highly polar biochars, produced at 400 °C, are rich in electron-withdrawing functional groups (Keiluweit et al., 2010). They tend to be electron-deficient and may act as π-acceptors towards electron donors. Both electron rich and poor functional groups are present in high temperature derived biochars; hence, they are theoretically capable of interacting with both electron donors and electron accepters (Sun et al., 2012). The π–π electron donor–acceptor interaction between π-electron rich graphene surface of biochar and π-electron deficient positively charged organics is enhanced (Qiu et al., 2009; Teixidó et al., 2011; Sun et al., 2012). However, an electrostatic repulsion between negatively charged anionic organic compounds and biochars could promote H-bonding and induce adsorption. This phenomenon was reported by Teixidó et al. (2011) who showed the sulfamethazine adsorption on hardwood derived biochar produced at 600 °C. It was postulated that anionic sulfamethazine deprotonates under alkaline conditions, which released OH^- and resulted in the formation of strong H-bonding between sulfamethazine and carboxylate or phenolate groups available on biochar (Teixidó et al., 2011).

Solution chemistry, such as pH and ionic strength, may also affect the sorption of organics onto biochar. The sorption capacity of biochars derived from crop residue at 350 °C for methyl violet increased sharply from pH 7.7 to 8.7 (Xu et al., 2011). The electrostatic attraction between biochars and methyl violet increased with the rise in pH due to the dissociation of phenolic –OH group of biochars, thereby increasing the net negative charge on their surfaces (Xu et al., 2011). Similarly, the ionic strength of the solution also showed positive effects on the organic contaminant adsorption on biochars (Qiu et al., 2009; Xu et al., 2011). In particular, an increase in anionic brilliant blue dye adsorption on biochars with an increase in ionic strength was due to neutralization of the negative charge of biochar with Na^+ and compression of electrical double layer near the surface, which effectively reduced the electrostatic repulsion between the anionic dye and the biochar surface (Qiu et al., 2009). Biochar contains variable charged (or pH-dependent charge) surfaces. An increase in pH on these surfaces results in an increase in the negative charge (Xu et al., 2011). The relative effect of ionic strength on the adsorption onto these surfaces is pH dependent. In general, the effect of ionic strength on adsorption onto biochar can be positive or negative depending on pH or the point of zero charge of the biochar (Bolan et al., 1999).

3.1.2. Contaminated soils

Limited studies are available on biochar applications to remediate the soils contaminated with organic pollutants as compared to water remediation (Table 3). Jones et al. (2011) evaluated the long-term biochar effect on soil contaminated with simazine. Strong simazine sorption into the micropores of biochar suppresses biodegradation and leaching of simazine into groundwater (Jones et al., 2011). A high application rate (25 t ha^{-1}) and small particle size (<2 mm) of biochar were most effective for simazine adsorption. Yang et al. (2010) and Yu et al. (2009) reported the similar findings in which the biochars produced from woodchips and cotton straw pyrolyzed at 850 °C resulted in a remarkable decrease in the dissipation of chlorpyrifos, carbofuran, and fipronil from soil due to their high sorption, which consequently reduced their bioavailability. Those authors also reported a pronounced decrease in the uptake of these pesticides by the plants grown in contaminated soils. Comparatively less efficiency was reported by the biochar produced at <450 °C. Low pesticide adsorption in soils may be attributed to the potential association of biochar with dissolved organic matter from soil, which could coat biochar particles, reducing the accessibility of pesticides to the sorption sites (Zhang et al., 2010). Sorption of atrazine onto the organic C content of biochar produced from dairy manure at 450 °C shows that the higher dissolved organic C content in soil may reduce atrazine sorption by blocking the biochar pores (Cao et al., 2011).

Overall, the biochars produced at higher temperatures exhibit higher sorption efficiency for organic contaminant remediation in soil and water. This is probably due to the high surface area and microporosity of biochars. Additional sorption mechanisms include electrostatic attractions between charged surfaces of biochars and ionic organic compounds. However, the partitioning and subsequent diffusion into the non-carbonized and carbonized fractions of biochar could be an effective sorption mechanism for non-ionic compounds. Therefore, the biochars should be produced under well-defined pyrolysis conditions. The biochar properties should also be carefully examined before the applications for the remediation of specific organic contaminants in soil or water.

3.2. Remediation of inorganic contaminants in soil and water

Inorganic contaminants, particularly metals in the environment, originate mostly from a range of anthropogenic sources, such as mining, smelting, metal finishing, fertilizers, animal manure, pesticides, leaded gasoline, battery manufacture, power plants, waste water, and sewage sludge (Adriano, 2001; Ok et al., 2011; Usman et al., 2012; Lim et al., 2013). Unlike organic contaminants, metals are non-biodegradable and their bioavailability makes them highly toxic to living organisms (Adriano, 2001; Zhang et al., 2013). Carbonaceous materials have been deliberately used for *in situ* remediation of metal contaminated soil and water (Park et al., 2011a). Biochar has recently been applied as a novel carbonaceous material to adsorb metals in soil and water. However, contradicting explanations on the mobility of metals within biochar have been reported (Beesley et al., 2010). Therefore, specific investigations into the mechanisms related to metal binding, transformation, and release are required.

3.2.1. Metal contaminated waters

Heavy metal removal studies using biochar together with advanced spectroscopic techniques have recently been conducted to elucidate the adsorption capacities and binding mechanisms in aqueous media (Ippolito et al., 2012). Table 4 summarizes the recent studies on biochar applications for remediating soil and water contaminated with metals. Lima et al. (2010) compared eight different biochars derived from broiler litter, alfalfa stems, switch grass, corn cobs, corn stover, guayule bagasse, guayule shrubs, and soybean straw with their activated counterparts for their ability to adsorb Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} from water. Activated biochars were better metal adsorbents due to their high surface area and easy access to their functional groups. Copper showed greater affinity to biochars compared to other divalent metals, which may be attributed to the formation of surface complexes between Cu^{2+} and active functional groups (–COOH and –OH) on the biochars (Tong et al., 2011). Furthermore, an X-ray absorption fine structure (XAFS) spectroscopic investigation predicted that Cu^{2+} sorption onto biochar is pH dependent (Ippolito et al., 2012). The authors concluded that Cu^{2+} is sorbed to the organic functional groups of biochar at pH 6 and 7, whereas of azurite ($Cu_3(CO_3)_2(OH)_2$) and tenorite (CuO) precipitate within the biochar at pH 8 and 9 (Ippolito et al., 2012). Atomic/ionic size of the metal is another parameter of concern while considering adsorption onto biochar. Generally, the smaller ionic radius of metals, the greater adsorption capacity due to enhanced penetration into biochar pores (Ko et al., 2004; Ngah and Hanafiah, 2008).

The overall mechanisms of biochar interactions with metals are summarized in Fig. 3. Mechanisms for Pb^{2+} sorption by a sludge-derived biochar in an aqueous system were explained well by Lu et al. (2012). Four different possible mechanisms were proposed: (i) electrostatic outer-sphere complexation due to metal exchange with K^+ and Na^+ available in the biochar, (ii) co-precipitation and inner-sphere complexation of metals with organic matter and mineral oxides of the biochar, (iii) surface complexation with active carboxyl and hydroxyl functional groups of the biochar, and (iv) precipitation as lead–phosphate–silicate ($5PbO{\cdot}P_2O_5{\cdot}SiO_2$). Precipitation of Pb^{2+} with phosphate in water on dairy manure-derived biochar (enriched with P) has also been reported by Cao and Harris (2010). Similar to Cu and Pb, water soluble Hg can be precipitated as $Hg(OH)_2$ or $HgCl_2$ on alkaline biochar surfaces containing high chloride content (Kong et al., 2011). Sorption of Cr(VI) on biochars has been attributed to binding with negatively charged biochar active sites after its reduction to Cr(III) due to O-containing functional groups (Dong et al., 2011; Choppala et al., 2012; Bolan et al., 2013b). Mohan et al. (2011) demonstrated that the swelling behavior of oak wood and oak bark chars produced by fast pyrolysis is responsible for the high adsorption capacity for Cr(VI). Swelling of biochar in water opens the closed pores pre-existing in the dry biochar and provides more internal surface for adsorption. Furthermore, when wood is subjected to fast pyrolysis, the resulting char contains substantial (8–12%) oxygen. By-products of lignin pyrolysis include catechol and substituted catechol. Such structures must be present in the char and they generally act as reducing agents while being oxidized to ortho-quinone structural units. These units also chelate metal cations. As discussed by Mohan et al. (2011), celluloses and hemicelluloses also provide unsaturated anhydrosugars, diols, and other compounds that can reduce Cr(VI). Thus, these pyrolytic chars can readily reduce and bind to Cr(VI). As a result, biochar is an effective reductant for Cr(VI) due to its reactive surface functional groups and large surface area (Hsu et al., 2009a,b). The dominating mechanism for Cr(VI) adsorption on biochar has been suggested to consist of two parts: (i) the sorption of Cr(VI) and (ii) the subsequent reduction of sorbed Cr(VI) to Cr(III) (Hsu et al., 2009a). Aqueous Cr(VI) is possibly reduced by the formation of carboxylic and hydroxyl moieties available on biochar surfaces. The disordered polycyclic aromatic hydrocarbons sheets donate π-electrons for the Cr(VI) to be reduced (Wang et al., 2010). Cr(III) can then be adsorbed again by surface complexation and precipitation processes (Hsu et al., 2009a). Therefore, biochar enhances the reduction of toxic hexavalent Cr(VI) to less toxic trivalent Cr(III) in water.

3.2.2. Metal contaminated soils

Biochar can have a different effect on the mobility of metals in soils compared to that in water. Beesley et al. (2010) applied hardwood-derived biochar to multi-element (As, Cu, Cd, and Zn) contaminated soil. Interestingly, Cu and As are mobilized, whereas Cd and Zn are immobilized in soils amended with biochar as compared to un-amended soil. Copper leaching is associated with high dissolved organic C contents at the increased pH induced by applying biochar, whereas As leaching was attributed to increasing the

Table 4
Biochar utilization for inorganic contaminants remediation in soil and water.

Contaminant	Biochar type	Matrix	Effect	References
Arsenic	Hard wood (400 °C)	Soil	Mobilization due to enhanced pH and DOC	Hartley et al. (2009)
Arsenic and copper	Hard wood	Soil	Mobilization due to enhanced pH and DOC	Beesley et al. (2010)
Arsenic, cadmium, chromium, cobalt, copper, nickel, lead and zinc	Sewage sludge (500–550 °C)	Soil	Immobilization of arsenic, chromium, cobalt, nickel and lead due to rise in soil pH; mobilization of copper, zinc and cadmium due to high available concentrations in biochar	Khan et al. (2013b)
Cadmium and zinc	Hard wood	Soil	Immobilization due to enhanced pH	Beesley et al. (2010)
Cadmium, copper and lead	Chicken manure and green waste (550 °C)	Soil	Immobilization due to partitioning of metals from the exchangeable phase to less bioavailable organic-bound fraction	Park et al. (2011a)
Chromium	Oak wood (400–450 °C) Oak bark (400–450 °C)	Water	Sorption	Mohan et al. (2011)
Chromium	Sugar beat tailing (300 °C)	Water	Electrostatic attraction; reduction of Cr(VI) to Cr(III); complexation	Dong et al. (2011)
Copper	Broiler litter (700 °C)	Soil	Cation exchange; electrostatic interaction; sorption on mineral ash contents; complexation by surface functional groups	Uchimiya et al. (2011)c
Copper	Crop straw (400 °C)	Water	Adsorption due to surface complexation	Tong et al. (2011)
Copper	Pecan shell (800 °C)	Water	Sorption on humic acid at pH 6; precipitation of azurite or tenorite at pH 7, 8 and 9	Ippolito et al. (2012)
Copper and lead	Oak wood	Soil	Complexation with phosphorous and organic matter	Karami et al. (2011)
Copper and zinc	Hardwood (450 °C) Corn straw (600 °C)	Water	Endothermic adsorption	Chen et al. (2011b)
Copper, cadmium, nickel and zinc	Broiler litter (500 °C) Alfalfa stems (500 °C) Switch grass (500 °C) Corn cob (500 °C) Corn stover (500 °C) Guayule bagasse (500 °C) Guayule shrubs (500 °C) Soybean straw (500 °C)	Water	Adsorption onto inorganic fraction of biochar	Lima et al. (2010)
Lead	Dairy manure (450 °C)	Soil	Immobilization by hydroxypyromorphite formation	Cao et al. (2011)
Lead	Dairy manure (200 °C)	Water	Precipitation with phosphate	Cao and Harris (2010)
Lead	Oak wood (400 °C)	Soil	Immobilization by rise in soil pH and adsorption onto biochar	Ahmad et al. (2012b)
Lead	Rice straw	Soil	Non-electrostatic adsorption	Jiang et al. (2012)
Lead, copper, zinc and antimony	Broiler litter (350 and 600 °C)	Soil	Stabilization of Pb and Cu; desorption of Sb	Uchimiya et al. (2012)
Lead	Sewage sludge (550 °C)	Water	Adsorption due to cation release, functional groups complexation, surface precipitation	Lu et al. (2012)
Mercury	Soybean stalk (300–700 °C)	Water	Precipitation, complexation and reduction	Kong et al. (2011)
Nickel, copper, lead and cadmium	Cottonseed hulls (200–800 °C)	Soil	Surface functional groups of biochars controlled metal sequestration	Uchimiya et al. (2011b)

soil pH to 7.56. Similarly, Park et al. (2011a) reported Cu mobility in soil due to increased dissolved organic C with the addition of chicken manure-derived biochar. In contrast, the high pH induced by biochar results in reduced solubility of Cd and Zn. Increased mobility of As with biochar in soil was also reported by Hartley et al. (2009), and has been attributed to the rise in soil pH as well

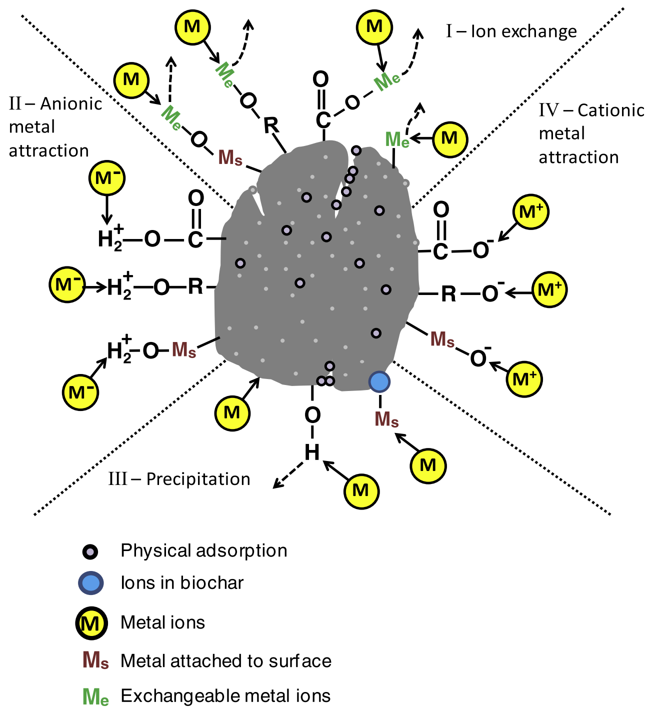

Fig. 3. Postulated mechanisms of biochar interactions with inorganic contaminants. Circles on biochar particle show physical adsorption. I – ion exchange between target metal and exchangeable metal in biochar, II – electrostatic attraction of anionic metal, III – precipitation of target metal, and IV – electrostatic attraction of cationic metal.

as As competition with soluble P in biochar. Biochar can also reduce As(V) to As(III), thereby enhancing As mobility (Park et al., 2011b; Zhang et al., 2013). Another oxyanion, Sb, also shows higher mobility in soil treated with broiler litter-derived biochar (Uchimiya et al., 2012). The electrostatic repulsion between anionic Sb and negatively charged biochar surfaces could have resulted in desorption of Sb. Conversely, the electrostatic attraction between positively charged Cu and negatively charged biochar is the prevailing mechanism of Cu immobilization in San Joaquin soil (Uchimiya et al., 2011c). Notably, Cu mobility/immobility is highly influenced by biochar organic C content. Generally, the biochars produced at <500 °C have high dissolved organic C content, which could facilitate the formation of soluble Cu complexes with dissolved organic C, as reported by Beesley et al. (2010) and Park et al. (2011a). Additionally, dissolved organic C can block the pores of biochars preventing Cu sorption (Bolan et al., 2010; Cao et al., 2011). However, the biochars produced at high temperatures (>600 °C) are generally deficient in dissolved organic C, which could affect Cu immobility in soil, as reported by Uchimiya et al. (2011c).

The effect of pyrolysis temperature on the retention of Pb by broiler litter-derived biochars produced at 350 and 650 °C was recently evaluated by Uchimiya et al. (2012). Those authors reported that biochar produced at a low pyrolysis temperature is favorable for immobilizing Pb. The increased release of available P, K, and Ca from biochars produced at a low temperature is associated with high Pb stabilization. Cao et al. (2011) demonstrated by XRD analysis that biochar derived from dairy manure containing a high amount of available P immobilized Pb in shooting range soil by forming insoluble hydroxypyromorphite ($Pb_5(PO_4)_3(OH)$). The role of O-containing functional groups on biochar surfaces towards metal binding was predicted by Uchimiya et al. (2011b), who reported that cottonseed hull-derived biochar produced at 350 °C contains high O content resulting in high uptake of Cu, Ni, Cd, and Pb.

Soil pH is considered to greatly influence the mobility of metals. Generally biochar is alkaline, thereby inducing liming effect in soil and causes immobilization of metals and mobilization of oxyanions (Almaroai et al., 2013). As discussed earlier, biochar-induced increases in soil pH can also influence the sorption of metals. For instance, Ahmad et al. (2013) reported that in soil amended with biochar, rise in soil pH favored the sorption of Pb onto kaolinite making charge on kaolinite more negative. At $pH > 5$, Pb forms strong inner sphere bidentate surface complexes with kaolinite (Gräfe et al., 2007).

Biochar shows the potential to mitigate Cr contaminated soils as they are highly reactive with many functional groups and are able to donate electrons (Choppala et al., 2012). The increase in proton supply for Cr(VI) reduction may be attributed to the presence of several O-containing acidic (carbonyl, lactonic, carboxylic, hydroxyl, and phenol) and basic (chromene, ketone, and pyrone) functional groups (Goldberg, 1985; Boehm, 1994). The resulting Cr(III) either adsorbs or participates in surface complexation with organic amendments (Hsu et al., 2009a). However, high pH biochars may prevent dissociation and oxidation of phenolic and hydroxyl groups, which may limit the supply of protons for reducing Cr(VI) (Choppala et al., 2012). Moreover, soil microbes can also cause the reduction of Cr(VI) to Cr(III) using C as an energy source from the biochar (Zimmerman, 2010). Because of the lower solubility of Cr(III) than Cr(VI), this reduction eventually results in immobilizing the Cr, thereby diminishing mobility and transport (Choppala et al., 2012).

The effect of biochar on remediation of soil and water co-contaminated with organic and inorganic contaminants has received little attention. Cao et al. (2011) reported the simultaneous immobilization of Pb and atrazine by dairy-manure biochar in soil. Those authors demonstrated that Pb was immobilized as a result of precipitation to insoluble hydroxypyromorphite due to the P content in the biochar, whereas atrazine was adsorbed onto biochar surfaces. The sorption phenomenon of co-existing organic and inorganic contaminants in aqueous solution is more complex. For example, biochar derived from soybean stalks works well for the phenanthrene and Hg(II) adsorption in a single component system, however direct competitive sorption is suppressing in a binary component system (Kong et al., 2011). The decrease in the effective surface area of biochar due to pore blockage by insoluble Hg(II) compounds results in a decrease in phenanthrene adsorption (Kong et al., 2011). In contrast, Chen et al. (2007) discounted the pore blockage mechanism for direct competitive adsorption between Cu and organic compounds (naphthalene, dichlorobenzene, and dichlorophenol) in an aqueous system. They speculated that the strong inner-sphere complexation between metal and biochar surfaces results in inhibiting organic compound adsorption around the metal-complexed moieties.

It is worth noting that sorption of organic contaminants by biochars is more favored than that of inorganic contaminants. Kong et al. (2011) reported 99.5% removal efficiency of phenanthrene by soybean stalk based biochar compared to 86.4% removal of Hg(II) from aqueous solution. This greater sorption capacity of biochar for organic contaminants is attributable to their high surface area and microporosity (Table 3). Contrarily, ion-exchange, electrostatic attraction and precipitation are prevailing mechanisms for the remediation of inorganic contaminants by biochar (Fig. 3). Since, the sorption of organic contaminants depends mainly on surface area and pore size, biochar in general shows greater sorption capacity for organic than inorganic contaminants.

The physicochemical properties of biochars as affected by pyrolysis temperature greatly influence their sorption efficiencies for both organic and inorganic contaminants. Biomass pyrolyzed at a high temperature is more effective for organic contaminants due to the high surface area and developed pore structures, whereas low temperature pyrolyzed biomass is efficient for inorganic contaminants due to the presence of more O-containing functional groups and the greater release of cations. The specific type of contaminant also impacts sorption properties of the biochar. Polar and non-polar, ionic and non-ionic organic contaminants have different affinities for biochars compared to those of cationic and anionic metals. Therefore, all biochars are not equally effective for sorbing contaminants, and care should be taken before applying biochar to remediate contaminated soil or water on a large scale. Research on biochar is contemporary, and still needs in-depth investigations to determine the long-term effects of biochar applied to contaminated areas.

4. Summary

Biochar has the potential to remediate soil and water contaminated with various organic/inorganic contaminants. Studies have demonstrated the biochar capability to serve as a green environmental sorbent. However, one type of biochar may not be appropriate for all contaminants removal. A number of variables are involved in determining the exact role of a biochar for environmental management. Pyrolysis condition and feedstock type are the main factors influencing biochars sorption behavior. The complex nature of soil systems compared to aquatic systems has limited biochar applications to soil.

Investigations have shown that biochar could increase the mobility of some toxic metals (particularly anionic metals) in soils. Therefore, the examination of the biochar efficacy on the mobility/stabilization of contaminants in multi-element contaminated soils should be carried out. It is also important to predict the metal stabilization mechanism of biochar to determine the long-term effectiveness of the remediation technology. In this respect, the recent research has been performed using state-of-the-art analytical techniques such as XAFS spectroscopy. Moreover, long-term field experiments on biochar application to contaminated soils are needed. The distinct physical architecture and molecular composition of biochar will be helpful in determining its long-term functions in soil and water.

Undoubtedly, the biochar use as an environmental sorbent can have strong implications. For example, activated biochar could replace activated carbon, as it has equivalent or even greater sorption efficiency for various contaminants due to its cost-effective production from waste resources such as agricultural wastes. This would make biochar less expensive compared to activated carbon. The estimated break-even price for biochar is US \$246 t^{-1}, which is approximately 1/6 of commercially available activated carbon (~US \$1500 t^{-1}) (McCarl et al., 2009; Ahmad et al., 2012a). Converting waste biomass into biochar will also promise an effective solution for the safe and beneficial disposal of a number of materials. In particular, solid waste material such as animal litter and sewage sludge will be removed of all active pathogens through conversion to biochar. The evolved volatiles and gases can be captured and condensed into bio-oil and syngas during biochar production, which can be further used as a source of renewable energy. Applying biochar to remediate contaminated soil will additionally provide a means of C sequestration, leading climate change mitigation.

Acknowledgements

This study was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science and Technology (2012R1A1B3001409).

References

Adriano, D.C., 2001. Trace elements in terrestrial environments. Biogeochemistry, Bioavailability, and Risks of Metals. Springer, New York.

Ahmad, M., Lee, S.S., Dou, X., Mohan, D., Sung, J.K., Yang, J.E., Ok, Y.S., 2012a. Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. Bioresour. Technol. 118, 536–544.

Ahmad, M., Lee, S.S., Yang, J.E., Ro, H.M., Lee, Y.H., Ok, Y.S., 2012b. Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil. Ecotoxicol. Environ. Saf. 79, 225–231.

Ahmad, M., Usman, A.R.A., Lee, S.S., Kim, S.C., Joo, J.H., Yang, J.E., Ok, Y.S., 2012c. Eggshell and coral wastes as low cost sorbents for the removal of Pb^{2+}, Cd^{2+} and Cu^{2+} from aqueous solutions. J. Ind. Eng. Chem. 18, 198–204.

Ahmad, M., Lee, S.S., Lim, J.E., Lee, S.E., Cho, J.S., Moon, D.H., Hashimoto, Y., Ok, Y.S., 2014. Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. Chemosphere 95, 433–441.

Almaroai, Y.A., Usman, A.R.A., Ahmad, M., Moon, D.H., Cho, J.S., Joo, Y.K., Jeon, C., Lee, S.S., Ok, Y.S., 2013. Effects of biochar, cow bone, and eggshell on Pb availability to maize in contaminated soil irrigated with saline water. Environ. Earth Sci.. http://dx.doi.org/10.1007/s12665-013-2533-6.

Awad, Y.M., Blagodatskaya, E., Ok, Y.S., Kuzyakov, Y., 2012. Effects of polyacrylamide, biopolymer, and biochar on decomposition of soil organic matter and plant residues as determined by ^{14}C and enzyme activities. Eur. J. Soil Biol. 48, 1–10.

Awad, Y.M., Blagodatskaya, E., Ok, Y.S., Kuzyakov, Y., 2013. Effects of polyacrylamide, biopolymer and biochar on the decomposition of ^{14}C-labelled maize residues and on their stabilization in soil aggregates. Eur. J. Soil Sci. 64, 488–499.

Bargmann, I., Rilling, M.C., Buss, W., Kruse, A., Kuecke, M., 2013. Hydrochar and biochar effects on germination of spring barley. J. Agro. Crop Sci. 199, 360–373.

Barrow, C.J., 2012. Biochar: potential for countering land degradation and for improving agriculture. Appl. Geogr. 34, 21–28.

Beesley, L., Jiménez, E.M., Eyles, J.L.G., 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environ. Pollut. 158, 2282–2287.

Boehm, H.P., 1994. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon 32, 759–769.

Bolan, N.S., Naidu, R., Syers, J.K., Tillman, R.W., 1999. Surface charge and solute interactions in soils. Adv. Agron. 67, 87–140.

Bolan, N.S., Adriano, D., Senesi, N., Kunhikrishnan, A., James, T., McDowell, R., 2010. Dissolved organic carbon: biogeochemistry, dynamics and agro-environmental significance in soils. Adv. Agron. 110, 1–67.

Bolan, N.S., Thangarajan, R., Seshadri, B., Jena, U., Das, K.C., Wang, H., Naidu, R., 2013a. Landfills as a biorefinery to produce biomass and capture biogas. Bioresour. Technol. 135, 578–587.

Bolan, N.S., Choppala, G., Kunhikrishnan, A., Park, J.H., Naidu, R., 2013b. Microbial transformation of trace elements in soils in relation to bioavailability and remediation. Rev. Environ. Contaminat. Toxicol. 225, 1–56.

Bourke, J., Harris, M.M., Fushimi, C., Dowaki, K., Nunoura, T., Antal Jr., M.J., 2007. Do all carbonized charcoals have the same chemical structure? 2. A model of the chemical structure of carbonized charcoal. Ind. Eng. Chem. Res. 46, 5954–5967.

Brick, S., 2010. Biochar: Assessing the Promise and Risks to Guide US Policy. Natural Resource Defense Council, USA.

Brown, R., 2009. Biochar production technology. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management Science and Technology. Earthscans, UK, pp. 127–146.

Cantrell, K.B., Hunt, P.G., Uchimiya, M., Novak, J.M., Ro, K.S., 2012. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. Bioresour. Technol. 107, 419–428.

Cao, X., Harris, W., 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. Bioresour. Technol. 101, 5222–5228.

Cao, X., Ma, L., Liang, Y., Gao, B., Harris, W., 2011. Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. Environ. Sci. Technol. 45, 4884–4889.

Chan, K.Y., van Zweiten, L., Meszaros, I., Downie, A., Joseph, S., 2007. Assessing the agronomic values of contrasting char materials on Australian hardsetting soil. In: Proceedings of the Conference of the International Agrichar Initiative, 30 April–2 May, Terrigal, NSW, Australia.

Chen, B., Chen, Z., 2009. Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. Chemosphere 76, 127–133.

Chen, J., Zhu, D., Sun, C., 2007. Effect of heavy metals on the sorption of hydrophobic organic compounds to wood charcoal. Environ. Sci. Technol. 41, 2536–2541.

Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition on nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. Environ. Sci. Technol. 42, 5137–5143.

Chen, B., Chen, Z., Lv, S., 2011a. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. Bioresour. Technol. 102, 716–723.

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B., Hay, A.G., 2011b. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. Bioresour. Technol. 102, 8877–8884.

Cheng, C.H., Lehmann, J., Thies, J.E., Burton, S.D., 2008. Stability of black carbon in soils across a climatic gradient. J. Geophys. Res. 113, 1–10.

Choppala, G.K., Bolan, N.S., Mallavarapu, M., Chen, Z., Naidu, R., 2012. The influence of biochar and black carbon on reduction and bioavailability of chromate in soils. J. Environ. Qual. 41, 1–10.

Cowie, A.L., Downie, A.E., George, B.H., Singh, B., Zweiten, L.V., O'Connell, D., 2012. Is sustainability certification for biochar the answer to environmental risks? Pesqui. Agropecu. Brasil 47, 637–648.

Demirbas, A., Arin, G., 2002. An overview of biomass pyrolysis. Energy Source 24, 471–482.

Dong, X., Ma, L.Q., Li, Y., 2011. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. J. Hazard. Mater. 190, 909–915.

Downie, A., Crosky, A., Munroe, P., 2009. Physical properties of biochar. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management Science and Technology. Earthscans, UK, pp. 13–32.

Enders, A., Hanley, K., Whitman, T., Joseph, S., Lehmann, J., 2012. Characterization of biochars to evaluate recalcitrance and agronomic performance. Bioresour. Technol. 114, 644–653.

Glaser, B., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal – a review. Biol. Fertil. Soils 35, 219–230.

Goldberg, E.D., 1985. Black Carbon in the Environment: Properties and Distribution. John Wiley & Sons, New York.

Gräfe, M., Singh, B., Balasubramanian, M., 2007. Surface speciation of Cd(II) and Pb(II) on kaolinite by XAFS spectroscopy. J. Colloid Interf. Sci. 315, 21–32.

Hale, S.E., Hanley, K., Lehmann, J., Zimmerman, A.R., Cornelissen, G., 2011. Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. Environ. Sci. Technol. 45, 10445–10453.

Hartley, W., Dickinson, N.M., Riby, P., Lepp, N.W., 2009. Arsenic mobility in brownfield soils amended with green waste compost or biochar and planted with *Miscanthus*. Environ. Pollut. 157, 2654–2662.

Hsu, N.H., Wang, S.L., Lin, Y.C., Sheng, G.D., Lee, J.F., 2009a. Reduction of Cr(VI) by crop-residue-derived black carbon. Environ. Sci. Technol. 43, 8801–8806.

Hsu, N.H., Wang, S.L., Liao, Y.H., Huang, S.T., Tzou, Y.M., Huang, Y.M., 2009b. Removal of hexavalent chromium from acidic aqueous solutions using rice straw-derived carbon. J. Hazard. Mater. 171, 1066–1070.

IBI, 2012. Standardized product definition and product testing guidelines for biochar that is used in soil. International Biochar Initiative, April 2012.

Ippolito, J.A., Strawn, D.G., Scheckel, K.G., Novak, J.M., Ahmedena, M., Niandou, M.A.S., 2012. Macroscopic and molecular investigations of copper sorption by a steam-activated biochar. J. Environ. Qual. 41, 150–156.

Jeong, C.Y., Wang, J.J., Dodla, S.K., Eberhardt, T.L., Groom, L., 2012. Effect of biochar amendment on tylosin adsorption–desorption and transport in two different soils. J. Environ. Qual. 41, 1185–1192.

Jiang, T.-Y., Jiang, J., Xu, R.-K., Li, Z., 2012. Adsorption of Pb(II) on variable charge soils amended with rice-straw derived biochar. Chemosphere 89, 249–256.

Jones, D.L., Jones, G.E., Murphy, D.V., 2011. Biochar mediated alternations in herbicide breakdown and leaching in soil. Soil Biol. Biochem. 43, 804–813.

Karami, M., Clemente, R., Jimenez, E.M., Lepp, N.W., Beesley, L., 2011. Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. J. Hazard. Mater. 191, 41–48.

Karaosmanoğlu, F., Ergűdenler, A.I., Sever, A., 2000. Biochar from the straw–stalk of rapeseed plant. Energy Fuels 14, 336–339.

Kasozi, G.N., Zimmerman, A.R., Kizza, P.N., Gao, B., 2010. Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars). Environ. Sci. Technol. 44, 6189–6195.

Keiluweit, M., Nico, P.S., Johnson, M.G., Kleber, M., 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environ. Sci. Technol. 44, 1247–1253.

Khan, S., Wang, N., Reid, B.J., Freddo, A., Cai, C., 2013a. Reduced bioaccumulation of PAHs by *Lactuca satuva* L. grown in contaminated soil amended with sewage sludge and sewage sludge derived biochar. Environ. Pollut. 175, 64–68.

Khan, S., Chao, C., Waqas, M., Arp, H.P.H., Zhu, Y.G., 2013b. Sewage sludge biochar influence upon rice (*Oryza sativa* L.) yield, metal bioaccumulation and greenhouse gas emissions from acidic paddy soil. Environ. Sci. Technol. 47, 8624–8632.

Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., Schwanninger, M., Gerzabek, M.H., Soja, G., 2012. Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. J. Environ. Qual. 41, 990–1000.

Ko, D.C.K., Cheung, C.W., Choy, K.K.H., Porter, J.F., McKay, G., 2004. Sorption equilibria of metal ions on bone char. Chemosphere 54, 272–281.

Kong, H., He, J., Gao, Y., Wu, H., Zhu, X., 2011. Cosorption of phenanthrene and mercury(II) from aqueous solution by soybean stalk-based biochar. J. Agric. Food Chem. 59, 12116–12123.

Kuzyakov, Y., Subbotina, I., Chen, H., Bogomolova, I., Xu, X., 2009. Black carbon decomposition and incorporation into soil microbial biomass estimated by ^{14}C labeling. Soil Biol. Biochem. 41, 210–219.

Kwon, S., Pignatello, J.J., 2005. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): pseudo pore blockage by model lipid components and its implications for N_2-probed surface properties of natural sorbents. Environ. Sci. Technol. 39, 7932–7939.

Lee, J.W., Kidder, M., Evans, B.R., Paik, S., Buchanan III, A.C., Garten, C.T., Brown, R.C., 2010. Characterization of biochars produced from cornstovers for soil amendment. Environ. Sci. Technol. 44, 7970–7974.

Lehmann, J., 2009. Terra preta Nova – where to from here? In: Woods, W.I., Teixeira, W.G., Lehmann, J., Steiner, C., Prins, A.W. (Eds.), Amazonian Dark Earths: Wim Sombroek's Vision. Springer, Berlin, pp. 473–486.

Lehmann, J., Joseph, S., 2009. Biochar for environmental management: an introduction. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management Science and Technology. Earthscans, UK, pp. 1–12.

Lehmann, J., da Silva, J.P., Rondon, M., da Silva, C.M., Greenwood, J., Nehls, T., Steiner, C., Glaser, B., 2002. Slash-and-char: a feasible alternative for soil fertility management in the Central Amazon? In: 17th World Congress of Soil Science, 14–21 August, Thailand.

Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P., Krull, A.E., 2008. Australian climate–carbon cycle feedback reduced by soil black carbon. Nature Geosci. 1, 832–835.

Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Kockaday, W.C., Crowley, D., 2011. Biochar effects on soil biota – a review. Soil Biol. Biochem. 43, 1812–1836.

Li, D., Hockaday, W.C., Maseillo, C.A., Alvarez, P.J.J., 2011. Earthworm avoidance of biochar can be mitigated by wetting. Soil Biol. Biochem. 43, 1732–1737.

Lian, F., Huang, F., Chen, W., Xing, B., Zhu, L., 2011. Sorption of apolar and polar organic contaminants by waste tire rubber and its chars in single- and bi-solute systems. Environ. Pollut. 159, 850–857.

Libra, J.A., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., Titirici, M.M., Fühner, C., Bens, O., Kern, J., Emmerich, K.H., 2011. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. Biofuels 2, 89–124.

Lim, J.E., Ahmad, M., Usman, A.R.A., Lee, S.S., Jeon, W.T., Oh, S.E., Yang, J.E., Ok, Y.S., 2013. Effects of natural and calcined poultry waste on Cd, Pb and As mobility in contaminated soil. Environ. Earth Sci. 69, 11–20.

Lima, I.M., Boateng, A.A., Klasson, K.T., 2010. Physicochemical and adsorptive properties of fast-pyrolysis bio-chars and their steam activated counterparts. J. Chem. Technol. Biotechnol. 85, 1515–1521.

Lin, Y., Munroe, P., Joseph, S., Henderson, R., Ziolkowski, A., 2012. Water extractable organic carbon in untreated and chemical treated biochars. Chemosphere 87, 151–157.

Liu, Z., Zhang, F.S., Wu, J., 2010. Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment. Fuel 89, 510–514.

Liu, P., Liu, W.-J., Jiang, H., Chen, J.-J., Li, W.-W., Yu, H.-Q., 2012. Modification of bio-char derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution. Bioresour. Technol. 121, 235–240.

Lou, L., Wu, B., Wang, L., Luo, L., Xu, X., Hou, J., Xun, B., Hu, B., Chen, Y., 2011. Sorption and ecotoxicity of pentachlorophenol polluted sediment amended with rice-straw derived biochar. Bioresour. Technol. 102, 4036–4041.

Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., Qiu, R., 2012. Relative distribution of Pb^{2+} sorption mechanisms by sludge-derived biochar. Water Res. 46, 854–862.

McCarl, B.A., Peacocke, C., Chrisman, R., Kung, C.C., Sands, R.D., 2009. Economics of biochar production, utilization and greenhouse gas offsets. In: Lehmann, J., Joseph, A.S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, London, pp. 341–358.

Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 20, 848–889.

Mohan, D., Rajput, S., Singh, V.K., Steele, P.H., Pittman Jr., C.U., 2011. Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. J. Hazard. Mater. 188, 319–333.

Mullen, C.A., Boateng, A.A., Goldberg, N.M., Lima, I.S., Laird, D.A., Hicks, K.B., 2010. Bio-oil and bio-char production from corn cobs and stover by pyrolysis. Biomass Bioenergy 34, 67–74.

Ngah, W.S.W., Hanafiah, M.A.K.M., 2008. Removal of heavy metal ions from wastewater by chemically modified plant waste as adsorbents: a review. Bioresour. Technol. 99, 3935–3948.

Ok, Y.S., Usman, A.R.A., Lee, S.S., Abd El-Azeem, S.A.M., Choi, B., Hashimoto, Y., Yang, J.E., 2011. Effects of rapeseed residue on lead and cadmium availability and uptake by rice plants in heavy metal contaminated paddy soil. Chemosphere 85, 677–682.

Park, J.H., Choppala, G.K., Bolan, N.S., Chung, J.W., Cuasavathi, T., 2011a. Biochar reduces the bioavailability and phytotoxicity of heavy metals. Plant Soil 348, 439–451.

Park, J.H., Lamb, D., Paneerselvam, P., Choppala, G., Bolan, N., Chung, J.W., 2011b. Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. J. Hazard. Mater. 185, 549–574.

Petit, C., Kante, K., Bandosz, T.J., 2010. The role of sulfur-containing groups in ammonia retention on activated carbons. Carbon 48, 654–667.

Qiu, Y., Zheng, Z., Zhou, Z., Sheng, G.D., 2009. Effectiveness and mechanisms of dye adsorption on a straw-based biochar. Bioresour. Technol. 100, 5348–5351.

Raveendran, K., Ganesh, A., Khilar, K.C., 1995. Influence of mineral matter on biomass pyrolysis characteristics. Fuel 74, 1812–1822.

Ro, K.S., Cantrell, K.B., Hunt, P.G., 2010. High-temperature pyrolysis of blended animal manures for producing renewable energy and value-added biochar. Ind. Eng. Chem Res. 49, 10125–10131.

Saeed, A., Akhter, M.W., Iqbal, M., 2005. Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. Sep. Purif. Technol. 45, 25–31.

Salih, H.H., Patterson, C.L., Sorial, G.A., Sinha, R., Krishnan, R., 2011. The fate and transport of the SiO_2 nanoparticles in a granular activated carbon bed and their impact on the removal of VOCs. J. Hazard. Mater. 193, 95–101.

Shackley, S., Carter, S., Knowles, T., Middelink, E., Haefele, S., Sohi, S., Cross, A., Haszeldine, S., 2012. Sustainable gasification-biochar systems? A case-study of rice-husk gasification in Cambodia, Part 1: Context, chemical properties, environmental and health and safety issues. Energy Policy 42, 49–58.

Singh, B.P., Cowie, A.L., Smernik, R.J., 2012. Biochar carbon stability in a clayey soil as a function of feedstock and pyrolysis temperature. Environ. Sci. Technol. 46, 11770–11778.

Sohi, S.P., 2012. Carbon storage with benefits. Science 338, 1034–1035.

Sohi, S., Loez-Capel, S., Krull, E., Bol, R., 2009. Biochar's roles in soil and climate change: a review of research needs. CSIRO Land Water Sci. Rep. 05 (09), 64.

Sohi, S.P., Krull, E., Lopez-Capel, E., Bol, R., 2010. A review of biochar and its use and function in soil. In: Sparks, D.L. (Ed.), Advances in Agronomy. Academic Press, Burlington, pp. 47–82.

Sun, K., Keiluweit, M., Kleber, M., Pan, Z., Xing, B., 2011. Sorption of fluorinated herbicides to plant biomass-derived biochars as a function of molecular structure. Bioresour. Technol. 102, 9897–9903.

Sun, K., Jin, J., Keiluweit, M., Kleber, M., Wang, Z., Pan, Z., Xing, B., 2012. Polar and aliphatic domains regulate sorption of phthalic acid esters (PAEs) to biochars. Bioresour. Technol. 118, 120–127.

Teixidó, M., Pignatello, J.J., Beltrán, J.L., Granados, M., Peccia, J., 2011. Speciation of the ionizable antibiotic sulfamethazine on black carbon (biochar). Environ. Sci. Technol. 45, 10020–10027.

Tong, S.J., Li, J.Y., Yuan, J.H., Xu, R.K., 2011. Adsorption of Cu(II) by biochars generated from three crop straws. Chem. Eng. J. 172, 828–834.

Uchimiya, M., Wartelle, L.H., Lima, I.M., Klasson, K.T., 2010. Sorption of deisopropylatrazine on broiler litter biochars. J. Agric. Food Chem. 58, 12350–12356.

Uchimiya, M., Chang, S., Klasson, K.T., 2011a. Screening biochars for heavy metal retention in soil: role of oxygen functional groups. J. Hazard. Mater. 190, 432–441.

Uchimiya, M., Klasson, K.T., Wartelle, L.H., Lima, I.M., 2011b. Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations. Chemosphere 82, 1431–1437.

Uchimiya, M., Wartelle, L.H., Klasson, T., Fortier, C.A., Lima, I.M., 2011c. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. J. Agric. Food Chem. 59, 2501–2510.

Uchimiya, M., Bannon, D.I., Wartelle, L.H., Lima, I.M., Klasson, K.T., 2012. Lead retention by broiler litter biochars in small arms range soil: impact of pyrolysis temperature. J. Agric. Food Chem. 60, 5035–5044.

Usman, A.R.A., Lee, S.S., Awad, Y.M., Lim, K.J., Yang, J.E., Ok, Y.S., 2012. Soil pollution assessment and identification of hyperaccumulating plants in chromate copper arsenate (CCA) contaminated sites, Korea. Chemosphere 87, 872–878.

Verheijen, F., Jeffery, S., Bastos, A.C., van der Velde, M., Diafas, I., 2010. Biochar application to soils. A Critical Scientific Review of Effects on Soil Properties, Processes and Functions. European Commission, Italy.

Wang, X.S., Chen, L.F., Li, F.Y., Chen, K.L., Wan, W.Y., Tang, Y.J., 2010. Removal of Cr(VI) with wheat-residue derived black carbon: reaction mechanism and adsorption performance. J. Hazard. Mater. 175, 816–822.

Wardle, D.A., Nilsson, M.C., Zackrisson, O., 2008. Fire-derived charcoal causes loss of forest humus. Science 320, 629.

Weyers, S.L., Spokas, K.A., 2011. Impact of biochar on earthworm populations: a review. Appl. Environ. Soil Sci. 2011, 1–12.

Woolf, D., 2008. Biochar as a Soil Amendment: A Review of the Environmental Implications. <http://www.orgprints.org/13268/1/Biochar_as_a_soil_ amendment_-_a_review.pdf> (accessed on August, 2012).

Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J., Joseph, S., 2010. Sustainable biochar to mitigate climate change. Nat. Commun. 1, 1–56.

Xu, R.K., Xiao, S.C., Yuan, J.H., Zhao, A.Z., 2011. Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. Bioresour. Technol. 102, 10293–10298.

Xu, T., Lou, L., Luo, L., Cao, R., Duan, D., Chen, Y., 2012. Effect of bamboo biochar on pentachlorophenol leachability and bioavailability in agricultural soil. Sci. Total Environ. 414, 727–731.

Yang, X.B., Ying, G.G., Peng, P.A., Wang, L., Zhao, J.L., Zhang, L.J., Yuan, P., He, H.P., 2010. Influence of biochars on plant uptake and dissipation of two pesticides in an agricultural soil. J. Agric. Food Chem. 58, 7915–7921.

Yang, J.E., Skogley, E.O., Ok, Y.S., 2011. Carbonaceous resin capsule for vapor-phase monitoring of volatile monoaromatic hydrocarbons in soil. Soil Sediment Contam. 20, 205–220.

Yao, Y., Gao, B., Chen, H., Jiang, L., Inyang, M., Zimmerman, A.R., Cao, X., Yang, L., Xue, Y., Li, H., 2012. Adsorption of sulfamethoxazole on biochar and its impact on reclaimed water irrigation. J. Hazard. Mater. 209–210, 408–413.

Yu, X.Y., Ying, G.G., Kookana, R.S., 2009. Reduced plant uptake of pesticides with biochar additions to soil. Chemosphere 76, 665–671.

Yu, X., Pan, L., Ying, G., Kookana, R.S., 2010. Enhanced and irreversible sorption of pesticide pyrimethanil by soil amendment with biochars. J. Environ. Sci. 22, 615–620.

Yu, L., Tang, J., Zhang, R., Wu, Q., Gong, M., 2013. Effect of biochar application on soil methane emission at different soil moisture levels. Biol. Fertil. Soils 49, 119–128.

Zhang, H., Lin, K., Wang, H., Gan, J., 2010. Effect of *Pinus radiate* derived biochars on soil sorption and desorption of phenanthrene. Environ. Pollut. 158, 2821–2825.

Zhang, W., Wang, L., Sun, H., 2011. Modifications of black carbons and their influence on pyrene sorption. Chemosphere 85, 1306–1311.

Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J., Bolan, N.S., Pei, J., Huang, H., 2013. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environ. Sci. Pollut. Res.. http://dx.doi.org/10.1007/s11356-013-1659-0.

Zheng, W., Guo, M., Chow, T., Bennett, D.N., Rajagopalan, N., 2010. Sorption properties of greenwaste biochar for two triazine pesticides. J. Hazard. Mater. 181, 121–126.

Zimmerman, A.R., 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). Environ. Sci. Technol. 44, 1295–1301.

Zimmerman, A.R., Gao, B., Ahn, M.Y., 2011. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. Soil Biol. Biochem. 43, 1169–1179.

Zweiten, L.V., Singh, B., Joseph, S., Kimber, S., Cowei, A., Chan, K.Y., 2009. Biochar and emissions of non-CO_2 greenhouse gases from soil. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management Science and Technology. Earthscans, UK, pp. 227–250.

Zweiten, L.V., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S., Cowie, A., 2010. Effect of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant Soil 327, 235–246.