

Biochar: As An Absorbent For Organic And Inorganic Contaminants In Soil And Water-A Review

A.A.S.V. Gunatilake
Department of Geology
University of Peradeniya
Peradeniya, Sri Lanka
Email;vidusumitha@gmail.com

S.K.Gunatilake
Department of Natural Resources,
Sabaragamuwa University of Sri Lanka,
P.O.Box 2, Belihuloya, Sri Lanka
Email;sksg@appsc.sab.ac.lk

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. Since biochar has high organic C content, it has the potential to serve as a soil conditioner to improve the physicochemical and biological properties of soils. Specifically, the extent of O-containing carboxyl, hydroxyl, and phenolic surface functional groups in biochar could effectively bind soil contaminants. These multi-functional characteristics of biochar show the potential as a very effective environmental sorbent for organic and inorganic contaminants in soil and water.

Keywords— *biochar; absorption; pyrolysis; contaminants*

I. INTRODUCTION

Biochar is a newly constructed scientific term. It is a stable carbon-rich by-product synthesized through pyrolysis carbonization of plant- and animal-based biomass. 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”. Verheijen et al. (2010) defined biochar as “biomass that has been pyrolyzed in a zero or low oxygen environment”. 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). Presently use of waste biomass for biochar production is processed giving an economical benefit. 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). The benefits mainly including energy production and climate change mitigation (Barrow, 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).

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. Relatively high pyrolysis temperatures generally produce biochar 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. In this review, a succinct overview of current biochar use as a sorbent for contaminant management in soil and water is summarized and discussed.

II SPECIAL CHARACTERISTICS OF BIOCHAR

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). 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.

TABLE 1 CHARACTERISTICS OF BIOCHAR PRODUCED FROM DIFFERENT FEEDSTOCK

Feedstock	Pyrolysis temperature °C	Heating rate °C/min ⁻¹	Ash content (%)	pH	C,%	H, %	O, %	N,%	Surface area (m ² /g ⁻¹)	Pore volume cm ³ /g ⁻¹	References
Boiler litter	350	-	-	-	45.60	4.00	18.30	4.50	60.0	0.000	Uchimiya et al. (2010)
Buffalo weed	300	7.0	20.4	8.7	78.09	4.26	7.44	10.21	4.0	0.010	Unpublished data
Chicken litter	620	13.0	-	53.2	41.50	1.20	0.70	2.77	-	-	Ro et al. (2010)
Corn cobs	500	-	13.3	7.8	77.60	3.05	5.11	0.85	0.0	-	Mullen et al.(2010)
Corn stover	450	-	58.0	-	33.20	1.40	8.60	0.81	12.0	-	Lee et al. (2010)
Cotton seed hull	200	-	3.1	-	51.90	6.00	40.50	0.60	-	-	Uchimiya et al. (2011a)
Feed lot	700	8.3	44.0	10.3	52.41	0.91	7.20	1.70	145.2	-	Cantrell et al.(2012)
Fescue straw	200	-	5.7	-	47.20	7.11	45.10	0.61	3.3	-	Keiluweit et al. (2010)
Fescue straw	700	-	19.3	-	94.2	1.53	3.60	0.70	139.0	-	Keiluweit et al. (2010)
Oak bark	450	-	11.1	-	71.25	2.63	12.99	0.46	1.9	1.060	Mohan et al. (2011)
Orange peel	150	-	0.5	-	50.60	6.20	41.00	1.75	22.8	0.023	Chen and Chen (2009)
Orange peel	700	-	2.8	-	71.60	1.76	22.20	1.72	201.0	0.035	Chen and Chen (2009)
Peanut shell	700	7.0	8.9	10.6	83.76	1.75	13.34	1.14	448.2	0.200	Ahmad et al.(2012b)
Pine needles	100	-	1.1	-	50.87	6.15	42.27	0.71	0.7	-	Chen et al. (2008)
Pine needles	600	-	2.8	-	85.36	1.85	11.81	0.98	206.7	0.076	Chen et al.(2008)
Pine shaving	400	-	1.1	-	74.10	4.95	20.90	0.06	28.7	-	Keiluweit et al. (2010)
Pine wood	700	10.0	38.8	6.6	95.30	0.82	3.76	0.12	29.0	0.130	Liu et al.(2010)
Poultry litter	350	2.5	30.7	8.7	51.07	3.79	15.63		4.45	3.9	Cantrell et al. (2012)
Rice rusk	500	-	42.2	-	42.10	2.20	12.10	0.50	34.4	0.028	Liu et al. (2012)
Saw dust	450	-	1.1	5.9	72.00	3.50	24.41	0.08	-	-	Lin et al. (2012)
Saw dust	550	-	2.8	12.1	85.00	1.00	13.68	0.30	-	-	Lin et al. (2012)
Soyabean stover	300	7.0	10.4	7.3	68.81	4.29	24.99	1.88	5.6	-	Ahmad et al. (2012c)
Soyabean straw	400	20.0	-	-	44.10	-	-	2.38	-	-	Tong et al. (2011)
Swine solid	350	2.5	32.5	8.4	51.51	4.91	11.10	3.54	0.9	-	Cantrell et al. (2012)
Swine solid	700	8.3	52.9	9.5	44.06	0.74	4.03	2.61	4.1	-	Cantrell et al. (2012)
Swine solid	620	13.0	44.7	-	50.70	1.90	<0.01	3.26	-	-	Ro et al.(2010)
Tire rubber	600	10.0	15.6	-	81.30	1.67	1.43	-	51.5	0.120	Lian et al.(2011)

Pyrolysis temperature plays a significant role in changing biochar characteristics. Uchimiya et al. (2011a) converted cotton seed hulls into biochar at various pyrolysis temperatures ranging from 200 to 800°C. A rapid decrease in biochar yield was observed at 640°C due to the loss of volatile matter and non-condensable gases (CO₂, CO, H₂, and CH₄), whereas at >400°C, a steady biochar yield was observed. A rapid decline in biochar yield at <300°C was reported due to initial dehydration reactions.

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. Destruction of aliphatic alkyl and ester group, and exposure of the aromatic lignin core through higher pyrolysis temperatures may be responsible for an increase in surface area (Chen and Chen, 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 1). 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).

Since biochar has high organic C content, it 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% increases in the water holding capacity of soil containing biochar was reported (Glaser et al., 2002). Biochar generally has a neutral to alkaline pH. 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.

III BIOCHAR APPLICATION FOR SOIL AND WATER

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; Ahmad et al., 2012c). Currently, the activated carbon, which is charcoal that has been treated with oxygen to increase microporosity and surface area, is the most commonly used carbonaceous sorbent.

Biochar is quite similar to activated carbon with respect to mutual production via pyrolysis, with medium to high surface areas (Cao et al., 2011). 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 environment.

IV ABSORPTION OF ORGANIC CONTAMINANT IN SOIL AND WATER

Biochar is used in the organic contaminant removal in water treatment and soil remediation (Zhang et al., 2013). A greater proportion of biochar application studies focused on remediation of aqueous organic contaminants, whereas only a few studies are applicable to soil. 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). The various mechanisms proposed for the interaction of biochar with organic contaminants are summarized in Figure. 1. Partitioning or adsorption and electrostatic interactions between organic contaminants and biochar are critical for remediation applications and are discussed.

A. *Reaction with organic contaminants in water and biochar*

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 was the major sorption mechanism at low pyrolysis temperatures (100–300°C).

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. Polar compounds 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 (Sun et al., 2011). Therefore, the functionality of the target organic contaminant affects biochar adsorption capacity.

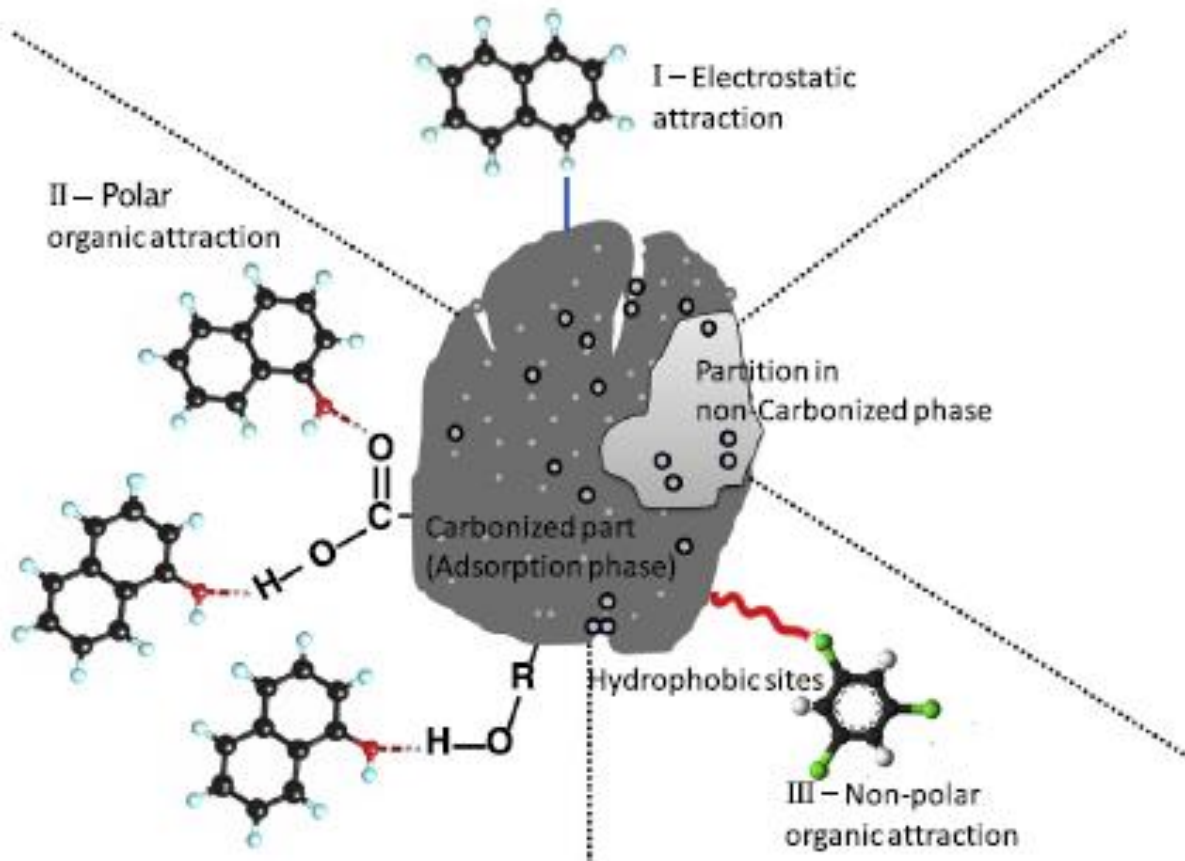


Figure 1 Postulated mechanisms of the interactions of biochar with organic contaminants. Circles on biochar particle show partition or adsorption. I – electrostatic interaction between biochar and organic contaminant, II – electrostatic attraction between biochar and polar organic contaminant, and III – electrostatic attraction between biochar and non-polar organic contaminant .(Ahmad et al. 2014)

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. 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 p-acceptors towards electron donors. Both electron rich and poor functional groups are present in high temperature derived biochar; hence, they are theoretically capable of interacting with both electron donors and electron acceptors (Sun et al.,2012). However, an electrostatic repulsion between negatively charged anionic organic compounds and biochar could promote H-bonding and induce adsorption.

In solution pH and ionic strength, may also affect the sorption of organics onto biochar. The electrostatic attractions between biochar and contaminants increase with the rise in pH. Similarly, the ionic strength of the solution also showed positive effects on the organic contaminant adsorption on biochar (Qiu et al., 2009; Xu et al., 2011). 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).

B. Reaction with organic contaminants in soil and biochar

Studies are limited available on biochar applications to remediate the soils contaminated with organic pollutants. Yang et al. (2010) and Yu et al. (2009) reported 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. 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).

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. 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.

TABLE 2 APPLICATION OF BIOCHAR FOR REMEDIATING CONTAMINATED SOIL AND WATER

Contaminant	Biochar type	Matrix	Effect	References
As & Cu	Hard wood	soil	Mobilization due to enhanced pH and DOC	Beesley et al. (2010)
As, Cd, Cr, Co, Cu, Ni, Pb and Zn	Sewage sludge (500-550C)	Soil	Immobilization of As, Cr, Co, Ni and Pb due to rise in soil pH; mobilization of Cu, Zn and Cd due to high available concentration in biochar	Khan et al. (2013)
Cd and Zn	Hard wood	Soil	Immobilization due to enhanced pH	Beesley et al. (2010)
Cd, Cu and Pb	Chicken manure and green waste (550C)	Soil	Immobilization due to partitioning of metals from the exchangeable phase to less bioavailable organic bound fraction	Park et al. (2011)
Cr	Oak wood (400-450C)	water	Sorption	Mohan et al. (2011)
Cr	Sugar beat talling (300C)	Water	Electrostatic attraction; reduction of Cr (VI) to CR(III); complexation	Dong et al. (2011)
Cu	Broiler litter (700C)	Soil	Cation exchange; electrostatic interaction; sorption on mineral ash contents; complexation by surface functional groups	Uchimiya et al.(2011)c
Cu	Crop straw (400C)	water	Adsorption due to surface complexation	Tong et al.(2011)
Cu	Pecan shell (800C)	water	Sorption on humic acid at pH 6; precipitation of azurite or tenorite at pH 7, 8 and 9	Ippolito et al.(2012)
Cu and Pb	Oak wood	Soil	Complexation with phosphorous and organic matter	Karami et al. (2011)
Cu and Zn	Hardwood (450C)	Water	Endothermic adsorption	Chen et al. (2011)
Cu, Cd, Ni and Zn	Broiler litter (500C)	Water	Adsorption onto inorganic fraction of biochar	Lima et al. (2010)
Pb	Dairy manure (200C)	Soil	Precipitation with phosphate	Cao and Harris (2010)
Pb	Rice straw	Soil	Non-electrostatic adsorption	Jiang et al. (2012)
Pb, Cu,Zn and Sb	Broiler litter (350 and 600C)	Soil	Stabilization of Pb and Cu; desorption of Sb	Uchimiya et al. (2012)
Pb	Sewage sludge (550C)	Water	Adsorption due to cation release, functional groups complexation, surface precipitation	Lu et al. (2012)
Hg	Soybean stalk (300-700C)	Water	Precipitation, complexation and reduction	Kong et al. (2011)

V. INORGANIC CONTAMINANTS IN SOIL AND WATER

Inorganic contaminants, particularly metals 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; Lim et al., 2013). Metals are non-biodegradable and their bioavailability makes them highly toxic to living organisms (Adriano, 2001). Biochar has recently been

applied as a novel carbonaceous material to adsorb metals in soil and water.

A. Reaction with inorganic contaminants in water and biochar

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 2 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 ($-\text{COOH}$ and $-\text{OH}$) on the biochars (Tong et al., 2011). 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 Figure. 2.

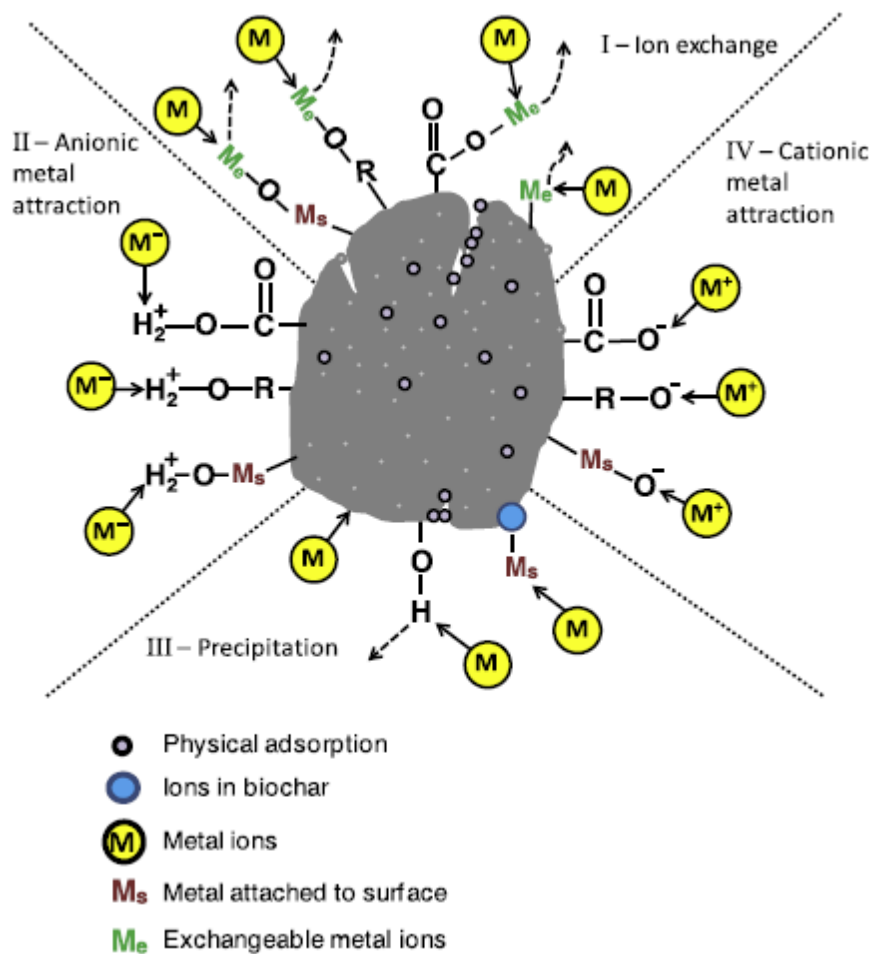


Figure 2 Postulated mechanisms of biochar interactions with inorganic contaminants.

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. (Ahmad et al. 2014)

B. Reaction with inorganic contaminants in soil and biochar

Biochar can have a different effect on the mobility of metals in soils compared to that in water. It is worth noting that sorption of organic contaminants by biochars is more favored than that of inorganic

contaminants. 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). However, the biochars produced at high temperatures ($>600^\circ\text{C}$) are generally deficient in dissolved organic C, which could affect Cu immobility in soil, as reported by

Uchimiya et al. (2011b). 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, lactic, carboxylic, hydroxyl, and phenol) and basic (chromene, ketone, and pyrone) functional groups (Goldberg, 1985; Boehm, 1994). 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). 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. Contrarily, ion-exchange, electrostatic attraction and precipitation are prevailing mechanisms for the remediation of inorganic contaminants by biochar (Figure 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.

Biochar 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 CO₂ emissions into the atmosphere (Cheng et al., 2008; Kuzyakov et al., 2009; Singh et al., 2012). Applying biochar together with organic or inorganic fertilizers can even enhance crop yields (Lehmann et al., 2002). Biochar accelerates the decomposition of soil native C by improving microbial populations (Kuzyakov et al., 2009) and the chemical hydrolysis by increasing soil pH (Yu et al., 2013). Increased microbial population and microbial activity in soils amended with biochar have also been observed (Verheijen et al., 2010; Lehmann et al., 2011). Li et al. (2011) recommended that a wet biochar application to soil could help mitigate avoidance of earthworms by preventing desiccation. A decrease of nutrient leaching due to biochar application has been also reported (Sohi et al., 2009).

A few recent studies have shown that biochar can reduce nitrous oxide (N₂O) and methane (CH₄) emissions from soil by both biotic and abiotic mechanisms (Zweiten et al., 2009). 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 CO₂-C equivalent emissions (Woolf et al., 2010). Also 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.

VI 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, several type of biochar may be needed 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. 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.

The biochar use as an environmental sorbent can have strong implications. Biochar can be used by replacing 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. 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.

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