

## Biochar as a Remediation for Heavy Metal Contaminated Soil : A Review

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### ABSTRACT

Soil contamination with heavy metals has increasingly become a serious global environmental issue in recent years. Waste emissions from industrial production, mining activities, waste water irrigation and other activities have increased the number of agricultural soils contaminated with heavy metals in many parts of the world. Soil contamination by heavy metals threatens the quality of agricultural production and human health, so it is necessary to choose certain economic and effective remediation techniques to control the continuous deterioration of land quality. Removal of heavy metals from contaminated soil is expensive and time consuming, so stabilization of heavy metals in situ by adding soil amendments such as lime, compost and biochar is commonly employed to reduce the bioavailability of heavy metals and minimize plant uptake. Biochar can potentially be used to reduce the bioavailability and leachability of heavy metals in soil. It has a large surface area, high capacity to adsorb heavy metals and is typically an alkaline material which can increase soil pH and contributes to stabilization of heavy metals in soil. Application of biochar for remediation of contaminated soils may provide a new solution to the soil pollution problem. In the present review, an attempt is made to summarise the work done on effects of biochar in remediating the heavy metal contaminated soils.

*Keywords:* Amendment, Bioavailability,  $\text{CaCl}_2$ -extractable heavy metals, pH

**H**EAVY metals are the metals with relatively high densities, atomic weights or atomic numbers (generally densities  $> 5 \text{ g cm}^3$ , atomic mass  $> 23$  or an atomic number  $> 20$ ). Some heavy metals are either essential nutrients (iron, cobalt and zinc) or relatively harmless (such as ruthenium, silver and indium), but can be toxic in larger amounts or certain forms. Other heavy metals, such as cadmium, mercury and lead are highly poisonous. Heavy metals are not biodegradable and persist for a long time in contaminated soils (Jiang *et al.*, 2012). Environmental pollution from hazardous metals and minerals can arise from natural as well as anthropogenic sources (Table 1). Natural sources are seepage from rocks into water, volcanic activity, forest fires etc. (Hu and Cheng, 2016). Anthropogenic sources are mainly due to waste emissions from industrial production, mining activities, waste (*i.e.*, biosolids and manures) application, waste water irrigation and inadequate management of pesticides and chemicals in agricultural production (Bolan *et al.*, 2004 and Mench *et al.*, 2010). Heavy metals are relatively scarce in the Earth's crust but are present in many aspects of

modern life. Soils contaminated with heavy metals pose a risk to the environment and to human health (Jiang *et al.*, 2012 and Lu *et al.*, 2014) due to biomagnification. Contamination of soils and crops with heavy metals may have adverse effects on soil, plants, animals and human beings (Hamsa and Prakash, 2018). Heavy metals also cause various toxic effects on the crop plants (Table 2). Hence, there is a need to remediate the heavy metal contaminated soil.

### Remediation of Heavy Metal Contaminated Soil

The heavy metal remediation techniques around the world mainly include physical, chemical, biological, agricultural ecology and joint remediation (Zhao *et al.*, 2015). It is expensive (physical and chemical remediation) and time consuming (biological remediation) to remove heavy metals from contaminated soils (Cui and Zhang, 2004). However, *in situ* chemical amendment of soil is an effective, time-saving, cost effective and environment friendly remediation method compared to others (Zhang *et al.*, 2011). Stabilisation of heavy metals in situ by adding soil amendments such as lime and compost is

TABLE 1  
Sources of heavy metals

Heavy metal	Anthropogenic source
Chromium (Cr)	Mining, industrial coolants, chromium salts manufacturing, leather tanning
Lead (Pb)	Lead acid batteries, paints, E-waste, smelting operations, coal-based thermal power plants, ceramics, bangle industry
Mercury (Hg)	Chlor-alkali plants, thermal power plants, fluorescent lamps, hospital waste, electrical appliances etc.
Arsenic (As)	Geogenic / natural processes, smelting operations, thermal power plants, fuel burning
Copper (Cu)	Mining, electroplating, smelting operations
Vanadium (Va)	Spent catalyst, sulphuric acid plant
Nickel (Ni)	Smelting operations, thermal power plants, battery industry
Cadmium (Cd)	Zinc smelting, waste batteries, e-waste, paint sludge, incinerations and fuel combustion
Molybdenum (Mo)	Spent catalyst
Zinc (Zn)	Smelting, electroplating

(Source: Gautam SP, CPCB, New Delhi)

commonly employed to reduce the bioavailability of metals and minimize plant uptake (Bolan and Duraisamy, 2003; Bolan *et al.*, 2004; Kumpiene, 2010 and Komarek *et al.*, 2013). Removal of heavy metals from soil and stabilization of heavy metals in soil to minimize their toxicity continues as important remediation approaches. On the other hand, metal stabilization through the processes of adsorption, binding or co-precipitation with amendments has been widely studied in the last decade (Kumpiene *et al.*, 2008) as it permits profitable and safe utilization of contaminated land (Clemente and Bernal, 2006).

Further more, increasing interest in integrating remediation and the provision of ecosystem services, such as carbon sequestration in soil, has provided an attractive land management option for contaminated sites using materials rich in carbon. Biochar, a carbonaceous solid derived from the pyrolysis (thermal decomposition of organic compounds at a relatively lower temperature (<700 °C) under limited supply of oxygen) of agricultural and forest residual biomass, has gained significant importance in recent days as a soil amendment because of its potential benefits in carbon sequestration in soil (Lehmann, 2007). Biochar can be produced from various feed stock materials or waste, such as agricultural residues, manures, industrial wastes etc. providing an alternative option for waste management (Rohitha *et al.*, 2021).

TABLE 2  
Toxic effects of heavy metals on crop plants

Heavy metals	Toxicity effects	References
Copper	Leaves chlorosis, change in ultrastructure	Viehweger ang geipel, 2010
Cadmium	Decrease in photosynthesis rate, root and shoot inhibition, membrane leakage	Hernandez and cooke, 1997
Aluminium	Change in ultrastructure of roots, lipid peroxidation	Kidd <i>et al.</i> , 2001
Lead	Change in composition of lipid, cellular concentrations of micronutrients changes	Viehweger ang geipel, 2010
Arsenic	Photosynthesis decreased, reduced transpiration intensity, electrolyte leakage	Singh <i>et al.</i> , 2006
Mercury	Reduced root elongation, transpiration rate, water uptake and chlorophyll synthesis	Sparks, 2005
Zinc	Reduction in germination percentage; reduced plant height and biomass; decrease in chlorophyll, sugar starch and amino acid content	Manivasagaperumal <i>et al.</i> , 2011

The mechanisms involved in immobilization of inorganic pollutants by biochar have been reviewed recently (Paz-Ferreiro *et al.*, 2014). Among these mechanisms, the contribution to pH changes was highly specific to biochar to decrease the mobility of the pollutant (Lu *et al.*, 2014 and Xing Yang *et al.*, 2015). Also, biochar is known to have a highly porous structure, high specific surface area and cation exchange capacity (Glaser and Birk, 2012) as well as various functional groups (Mumme *et al.*, 2011), leading to the assumption that biochar added to the soils may provide negatively charged surfaces for ion exchange that are responsible for the ability to sorb heavy metals. Park *et al.* (2011) reported that, the mechanisms responsible for elements immobilization by biochar include precipitation (*e.g.*, metal carbonates, phosphates and hydroxide precipitates), electrostatic interactions and surface chemi-sorption.

Stabilization of heavy metals in soils with application of biochar could involve a number of possible mechanisms, as illustrated in Fig. 1 (Lu *et al.*, 2012). Taking  $Pb^{2+}$  as an example, the authors proposed various mechanisms for  $Pb^{2+}$  sorption by sludge-derived biochar that could include (1) heavy metal exchange with  $Ca^{2+}$ ,  $Mg^{2+}$  and other cations associated

with biochar, attributing to co-precipitation and inner sphere complexation with complexed humic matter and mineral oxides of biochar; (2) the surface complexation of heavy metals with different functional groups and inner sphere complexation with the free hydroxyl of mineral oxides and other surface precipitation and (3) the physical adsorption and surface precipitation that contribute to the stabilization of  $Pb^{2+}$  (Lu *et al.*, 2012).

### Effect of Biochar on Soil Properties

Biochar alters some of the properties of soil like, pH, EC, OC, available nutrient content and some physical properties. Changes in the soil physico-chemical properties by the addition of biochar has an impact on mobility and bioavailability of heavy metals in soil. The rice straw biochar could be used as a substitution for lime material to increase the pH values (Xing Yang *et al.*, 2015). It is also likely that an increased pH also affects the metal mobility in soil (Lu *et al.*, 2014) by promoting the formation of precipitates, such as  $CdCO_3$ ,  $Cu(OH)_2$  and  $Pb_5(Po_4)_3OH$  (Cao *et al.*, 2011). The presence carbonates of alkali and alkaline earth metals, sesquioxide, silica and plant nutrients, particularly N, P, K and S, in ash residues of biochar might be the reason for increase in soil pH and EC (Clarholm, 1994 and Mahmood *et al.*, 2003). The pH, EC and OC contents are negatively correlated with available heavy metals in soil (Table 3). Application of biochar could increase the soil pH because of the releasing of basic compounds and base cations from biochar (Yuan *et al.*, 2010). Similar results were also found by Al-Wabel *et al.* (2015) and Hu *et al.* (2014) who reported that pH value of soil under Cd stress increased

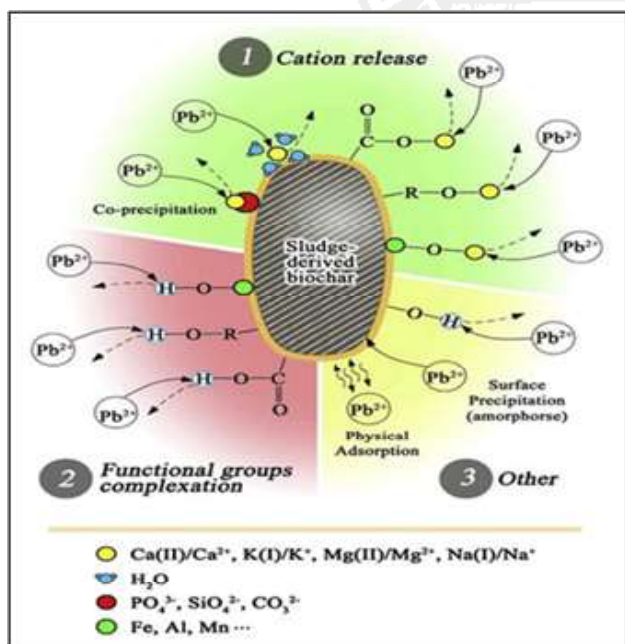


Fig. 1: Conceptual illustration of the possible mechanisms of Pb adsorption on biochar (from Lu *et al.*, 2012)

TABLE 3

Correlation coefficients between soil physicochemical properties and concentrations of extractable heavy metals (Xing Yang *et al.*, 2015)

	CaCl <sub>2</sub> - extractable heavy metals			
	Cd	Cu	Pb	Zn
pH	-0.749 <sup>b</sup>	-0.464 <sup>b</sup>	-0.920 <sup>b</sup>	-0.953 <sup>b</sup>
WSOC	-0.408 <sup>a</sup>	-0.464 <sup>b</sup>	-0.568 <sup>b</sup>	-0.558 <sup>b</sup>
Available P	-0.462 <sup>b</sup>	-0.631 <sup>b</sup>	-0.894 <sup>b</sup>	-0.922 <sup>b</sup>

after soil was added with biochar as compared to control. Application of pigeon pea biochar resulted in increase in soil pH from 8.12 to 8.19 (Vassanda Coumar *et al.*, 2015). Several investigations also showed that soil pH, EC and plant-available nutrients were increased as a result of biochar application (Amonette and Joseph, 2009; Warnock *et al.*, 2007 and Nigussie *et al.*, 2012).

Apart from pH, the key factors evaluating the quality of soil are EC, WSOC and CEC. These factors also affect the heavy metal behaviour in soil. Biochar is known to have a high content of water soluble organic carbon (WSOC). WSOC is the most mobile fraction of organic ligands and may promote the formation of heavy metal-organic complexes (Cao *et al.*, 2003). Vassanda Coumar *et al.* (2015) reported that, pigeon pea biochar application resulted in increase of soil organic carbon content from 0.43 to 0.70 per cent. Application of biochar at 2.5 and 5 g kg<sup>-1</sup> soil resulted in 34.9 and 60.5 per cent increase in soil organic carbon content respectively, over the soil receiving no biochar (0 g biochar kg<sup>-1</sup> soil).

### Effects of Biochar on Availability of Heavy Metals

Biochar can potentially be used to reduce the bioavailability and leachability of heavy metals in soil through increasing pH, adsorption and other physicochemical reactions. Increase in pH is found to be the main reason for reducing the availability of heavy metals in soil. The concentration of CaCl<sub>2</sub>-extractable heavy metals decreased with increasing addition of bamboo and rice straw biochar mainly due to increase in pH of soil by addition of biochar, extractable Cu, Pb and Zn reduced by 97.3, 97.9 and 62.2 per cent, respectively by the addition of five per cent application rate of fine rice straw biochar when compared to soil without any amendment (Xing Yang *et al.*, 2015). Chen *et al.* (2016) reported that the better reduction of heavy metals could also be accounted by the liming effect for raising pH of acid and slightly acid contaminated soil. Application rate and size of biochar applied also decides the heavy metal availability in soil, higher application rate and finer particle size were more effective because of the higher

surface area (Xing Yang *et al.*, 2015). Adsorption of heavy metals on biochar particles could also be the main mechanism in reducing heavy metal availability in soil, Vassanda Coumar *et al.* (2015) reported that biochar application had improved the overall sorption capacity of soil, significant reduction in DTPA-extractable (plant available fraction) cadmium was observed with increasing levels of biochar application, biochar addition at 2.5 and 5 g kg<sup>-1</sup> of soil decreased the extractability of cadmium by 27.2 and 41.1 per cent, respectively.

Similar findings were also observed by beesley *et al.* (2011) who observed that the application of biochar reduces the soil solution concentration of heavy metals by making stable organic matter complexes with heavy metals, by surface sorption of heavy metals on to different functional groups of biochar. Cd and Cu could also be almost as much as effectively fixed by biochar, the available Cd and Cu in soil added biochar decreased 18.8 and 18.6 per cent, respectively which proved biochar had better immobilization effect on heavy metals in acid soil, Biochar dose at two per cent decreased the Cd and Cu available fraction to 0.82 and 16.11 mg kg<sup>-1</sup>, respectively compared to 1.01 mg kg<sup>-1</sup> Cd and 19.79 mg kg<sup>-1</sup> Cu in the soil without any amendment, because biochar has large surface area with functional groups and generally high pH of biochar, which provide a convenient condition to immobilize heavy metal cations in soil through electrostatic and chelation between metals and biochar surface functional groups (Weili Jia *et al.*, 2017).

Application of biochar for remediation of contaminated soils may provide a new solution to the soil pollution problem, Biochar application is a more environmentally acceptable alternative to remediate the heavy metal contaminated soil, sorption mechanisms for metal contaminated soil by biochar could depend on the type of soil and the cations present in both soil and biochar, adsorption ability of the same type of biochar varies with different types of heavy metals. One type of biochar could not be universally used to remediate soils contaminated with various types of heavy metals, biochar can be used as an alternative of lime in increasing the pH of acid soils, biochar also has a

potential use in long term carbon sequestration and increasing soil fertility as well as promoting plant growth.

### Future Line of Work

1. Different mechanisms of immobilization of all toxic heavy metals with different type of biochar need to be studied.
2. Long term research on the effect of biochar on stabilization of heavy metals need to be done.
3. Specific feedstock biochar for effectively remediating a specific heavy metal contaminated soil need to be investigated.

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