SMART Biochar Technology for Remediation of Toxic Metals in Soils

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Abstract: Biochar is a carbon rich byproduct obtained from biomass pyrolysis. It has been known as a soil carbon enhancer or soil ameliorator. Heavy metal contamination is a serious concern in agricultural fields. Biochar showed significant positive impacts on heavy metal contaminated soils. Bioavailability of toxic metals such as Cd, Zn, Pb, Ni, and Cr can be reduced by biochar application into soils. Surface functional groups, cation exchange sites, and high porosity and surface area of biochar retain the heavy metals on its surface. However, some of toxic metals (Sb, As, Cu) demonstrated higher mobility in soils where biochar was applied. For instance, electrostatic repulsion between Sb and biochar surface enhances Sb mobility. High organic carbon content of biochar and reduction of As(VI) to As(III) can be factors increasing the mobility of Cu and As, respectively. All biochars are not equally effective for immobilizing metals in soils. Therefore, the development and selection of proper biochars is very important prior to its application on the large-scale contaminated sites. Research on biochar is contemporary and still needs in-depth investigations to determine the long-term effects of biochar. Therefore, smart biochar technology proposes a better or well-suitable way to remediate the soils contaminated with multi-metals via modification of typical biochar properties.

Keywords: Biochar, black carbon, heavy metals, soil remediation, immobilization, soil quality

1. Introduction

Biochar is defined as a carbon-rich product when biomass such as wood, manure or leaves is heated in a closed container with little or no available air (Lehmann and Joseph, 2009). In more technical terms, biochar is produced by so-called thermal decomposition of organic material under limited supply of O₂ at a relatively low temperature mostly below 700°C (Lehmann and Joseph, 2009). Because of its high organic C content, biochar has the potential to serve as a soil amendment to improve the physicochemical and biological properties of soils (Ahmad et al., 2014b).

Biochar is also recognized as a very significant tool of environmental management (Lehmann and Joseph, 2009). Further information on the concept of biochar is well reported in a pioneering review by Lehmann et al. (2006). 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).

Inorganic contaminants, particularly toxic 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; Lim et al., 2012; 2013). Unlike organic contaminants, those metals are non-biodegradable and their bioavailability makes them highly toxic to living organisms (Adriano, 2001; Abd El-Azeem et al., 2013; Ahmad et al., 2014b).

Numerous methods have been proposed to remediate toxic metals in soils. 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).

2. Biochar for remediation of toxic metals in soils

Beesley et al. (2010) applied a hardwood-derived biochar to multi-metals (arsenic [As], copper
[Cu], cadmium [Cd], and zinc [Zn]) contaminated soil. Interestingly, Cu and As were mobilized, whereas Cd and Zn are immobilized in soils amended with biochar as compared to un-amended soil. Copper leaching was associated with high dissolved organic C contents at the increased pH induced by applying biochar, whereas As leaching was attributed to increasing the soil pH to 7.56 (Almaroai et al., 2014).

Similarly, Park et al. (2011a) reported Cu mobility in soil due to increased dissolved organic C with the addition of a chicken manure-derived biochar. In contrast, the high pH induced by biochar results in reduced solubility of Cd and Zn (Ahmad et al., 2012a; 2012b; 2012c; 2012d).

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 as As competition with soluble P in biochar. Biochar can also reduce As(V) to As(III), thereby enhancing As mobility (Ahmad et al., 2014a; Almaroai et al., 2012; 2013a; Lim et al., 2014; Park et al., 2011b; Zhang et al., 2013).

Interestingly, reduced As availability has observed by Ahamd et al. (Fig. 1, unpublished data) in contaminated soils amended with pine needles-derived biochars pyrolyzed at 300 and 700°C. Hence, the type of feed stocks could be a determinant factor on soil As mobility.

![Exchangeable Pb and As](image1)

**Fig. 1.** Exchangeable (a) lead (Pb) and (b) arsenic (As), and TCLP (c) Pb and (d) As in soils treated with soybean stover biomass (S-BM), soybean stover-derived biochars pyrolyzed at 300°C (S-BC300) and 700°C (S-BC700), pine needles biomass (P-BM), and pine needles-derived biochars pyrolyzed at 300°C (P-BC300) and 700°C (P-BC700). Asterisk (*) shows concentration below detection limit (0.01 mg L⁻¹). Bars with the same letters above are not different at a 0.05 significance level (Ahamd et al. unpublished data).

Firing range soil treated with biochar showed reduced Pb mobility and enhanced antimony [Sb] mobility (Fig. 2) (Ahmad et al., 2012d; 2012e; 2014b; Hashimoto et al., 2013; Lee et al., 2013a; 2013b; Zhao et al., 2013). Oxyanion, Sb, also shows higher mobility in a soil treated with a 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., 2011b). Notably, Cu mobility/immobility is highly influenced by biochar organic C content (Awad et al., 2012; 2013; Moon et al., 2011; 2013). 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 (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. (2011a; 2011b).

Fig. 2. Exchangeable (a) lead (Pb) and (b) antimony (Sb) concentrations in firing range soils treated with mussel shell powder (MS), cow bone powder (CB) or biochar (BC). The same letters above each bar indicate no difference between treatments at a 0.05 significance level (adapted from Ahmad et al., 2014a).
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 (Mohan et al., 2014).

Cao et al. (2011) demonstrated by X-ray diffraction (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 (Pb₅(PO₄)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, nickel [Ni], Cd, and Pb.

Soil pH is considered to greatly influence the mobility of metals. Generally biochar is alkaline, thereby inducing a liming effect in soil and causes immobilization of metals and mobilization of oxyanions (Almaroai et al., 2013a; 2013b; 2014; Ok et al., 2007; Saifullah et al., 2014; Usman et al., 2012; 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 (Boehm, 1994; Goldberg, 1985). The resulting Cr(III) either adsorbs or participates in surface complexation with organic amendments. 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).

Ion-exchange, electrostatic attraction and precipitation are prevailing mechanisms for the remediation of inorganic contaminants by biochar (Fig. 3).
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 (adapted from Ahmad et al., 2014b).

3. Rice paddy soils

Heavy metal contamination in paddy soils is one of the most serious issues confronting rice production and soil management in Asian countries. Especially in Korea, the large paddy areas have been severely contaminated by Cd and Pb via effluent from mine tailings and other wastes generated by closed or abandoned mines (Ok et al., 2010; 2011a; 2011b; 2011c). As a result, accumulation of heavy metals into rice plants has produced a major environmental risk to human health (Vithanage et al., 2014; Yang et al., 2007; 2008).

Biochar showed a vital contribution to reduce the Cd and Pb bioavailability in contaminated paddy soils, while reducing the plant uptake and grain accumulation. A three years experiment conducted at a contaminated rice paddy in southern China single amended with wheat straw biochar showed a reduction of soil extractable Cd and Pb. Moreover, rice plant tissues’ Cd content was significantly reduced, depending on the biochar application rate. Root tissue Pb content also was found to decrease. Cd and Pb bonded with the aluminum (Al), iron (Fe) and phosphorus (P) on and around and inside of the biochar particles. Cation exchange sites on the porous carbon structure can also be a possible reason for the Pb and Cd immobilization in the contaminated paddy soil (Bian et al., 2014a). Similarly, Municipal biowaste biochar decreased the soil availability of Cd and grain Cd content during both rice
and wheat seasons in a rice paddy soil in eastern China (Bian et al., 2014b). Biochar soil amendment in a contaminated rice paddy in southern China was reduced rice grain Cd content by 20-90% (Bian et al., 2013). Reduced Cd bioavailability in soil and wheat grain Cd content following to the biochar application in a contaminated paddy soil have been also reported by Cui et al. (2012). In all these studies pH increment with biochar amendment was the critical reason for low Cd bioavailability and reduced plant uptake.

Interestingly, Cui et al. (2012) reported rice plant Cd uptake reduction in contaminated rice paddy in the second year compared to in the first year regarding to a single application of biochar as a basal in the first year. Hence, long term effect of biochar has profound its implication in contaminated paddy soils as a better bio-resource.

4. Smart biochar

Biochar surface modification or smart biochar production is concerned by scientists to improve the biochar qualities to use them in different areas (Sohi, 2012). Recently, the concept of engineered biochar has been used to various biochar composites for CO₂ sorption and environmental remediation (Yao et al., 2013; Zhang et al., 2012).

Biochar revealed promising results in toxic heavy metal remediation in contaminated soils. As explained above, biochar may increase the bioavailability of As, Cu and Sb. Hence, application of biochar for multi-metals contaminated soils may cause unexpected environmental problems. Song et al. (2014) used MnO₂ for biochar surface modification and it was demonstrated increased Cu²⁺ adsorption to the biochar surface. This enhanced Cu²⁺ adsorption was mainly due to the formation of inner-sphere complexes with MnO₂ and O containing groups on biochar surface. The stronger binding affinity of Cu²⁺ with MnO₂-loaded biochar was also helped for lower desorption rate relative to unmodified biochar. Surface modified biochar with Al(III) also showed better As(V) sorption under acidic condition than the unmodified biochar (Qian et al., 2013).

Smart biochar in metal remediation is still not employed well. Hence, smart biochar technology needs to be tested and used in metal remediation. It would be a possible scenario to remediate all types of metals in contaminated soils.

5. Conclusions

In recent years, biochar has been proposed as means of restoring or sequestering C within soil. The proposed benefits of biochar applications include the decreases of greenhouse gas (GHG) emissions, increases of nutrient and water retention of soils, stabilization of native soil organic matter, and decreases of the bioavailability of contaminants in soils. Biochar-induced immobilization of toxic metals in contaminated soils has recently received considerable attention. Despite the apparent benefits of biochar towards a variety of soil parameters, a fundamental knowledge of metal-biochar interactions is still lacking.

All biochars are not equally effective for immobilizing metals in soils. Therefore, the development and selection of proper biochars is very important prior to its application on the large-scale contaminated sites. Research on biochar is contemporary and still needs in-depth investigations to determine the long-term effects of biochar.

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7. References


