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Comparative Effects of Biochar, Slag and Ferrous–Mn Ore on Lead and Cadmium Immobilization in Soil

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Abstract

A variety of remediation approaches have been applied to the heavy metals-contaminated soils, however, the immobilization of metals in co-contaminated soils still not cleared. Therefore, an incubation study was conducted to evaluate the instantaneous effects of different concentrations of biochar (BC), slag (SL) and Fe–Mn ore (FMO) on immobilization of Pb and Cd through the Toxicity Characteristic Leaching Procedure (TCLP) by following the the European Community Bureau of Reference (BCR), $CaCl_2$ and NH_4NO_3. The sequential extraction of BCR showed decrease in acid soluble fractions, while the residual proportions of Pb and Cd were enhanced with increasing concentrations of SL and BC. Addition of BC significantly lowered the extractable fractions of both metals by TCLP, NH_4NO_3 and $CaCl_2$ as compared to SL and FMO. Among all amendments, BC incorporation into co-contaminated soil offered promising results for Pb and Cd immobilization. Overall, all amendments showed positive and long-term impact on the reclamation of co-contaminated soil with heavy metals and could deserve advance monitoring studies on a field scale.

Keywords Heavy metals · Immobilization · Bio-accessibility · Slag · Biochar · FMO

Soil contamination with variety heavy metals is alarming for the environment due to its harmful effects to food safety, animals and ultimately to human beings (Bian et al. 2013). The harmful impact is more severe in urban soils (Wong et al. 2006). Previously, various pathways have been indicated through which heavy metals end up in the food chain, including natural evolutionary geochemical activities, mining, spontaneous industrial developments and the metal refineries (Xu et al. 2013). It becomes very difficult to cope with the toxicity of heavy metals, once incorporated in the soil ecosystem (Jiang and Xu 2013). For the safe production of food, soil remediation approaches are required on an urgent basis to overcome the harmful impact of heavy metals. Among several remediation approaches for conservation of polluted soils (e.g. Soil washing, landfilling, and excavation), immobilization has been projected as a dynamic technique for the remediation of metal contaminated soils (Liang et al. 2014).

Among alkaline amendments used to reduce the negative effects of heavy metals in co-contaminated soils, biochar produced through pyrolysis of agro-based organic refusal under less oxygen condition (Lehmann 2007) is a novel approach. It has been previously confirmed that the toxicity level of heavy metals on plant and soil was minimized due to the greater affinity of biochar for heavy metals (Lu et al.

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2014). Due to the presence of dynamic functional groups on its surface as well as microporous structure, alkaline pH and higher CEC makes it very effective material for the immobilization of heavy metals (Xu et al. 2013). Moreover, the presence of oxygen-based functional groups on the surface of biochar stabilizes Pb and Cd in weathered acidic soils (Uchimiya et al. 2011). In addition, slag is a commonly used amendment, is a waste material generated from smelting of ore during the production of metals. This byproduct is normally used as cement or filler in the construction industry (Bing et al. 2016). The use of slag as an adsorbent for heavy metal removal has been proved to be economical as it reduces the volume of waste. Slags from different operations and industries contain a variety of compounds and minerals (TiO_2, Fe_2O_3, FeO, Fe_3O_4, BaO, MgO, CaO, MnO and SiO_2) at varying amounts which makes this a very good choice as adsorbents (Bing et al. 2016). The composition of slag can be practical to reclaim a number of toxic metals including Cd and Pb. The presence of Fe and Mn on these surfaces make these substances good electron acceptors or donors (Chen et al. 2011). While, the inactive state of ferrous manganese ore (FMO) influences various heavy metals immobilization in the contaminated soil. It is well documented that various compounds of metals in soil are difficult to remediate than sole metals, as it depicts environmental effects and collective interactions, creating the soil to remediate highly challengeable (Fang et al. 2012). Noticing these problems, the present study was designed to meet the following aims: (1) to assess the relative efficacy of different passivators on Pb and Cd in artificially co-contaminated soil, and (2) to assess the effect of passivators on Pb and Cd transformation and accessibility with the help of different tests (BCR, TCLP, $CaCl_2$ and NH_4NO_3).

Materials and Methods

The brown–red soil was sourced from the fields at Huazhong Agricultural University, Wuhan (30°28′N, 114°21′E), China and taken to the laboratory, air dried and sieved using 2 mm sieve before determination of pH and electrical conductivity (EC) in a soil/water (1:2.5 and 1:5, respectively). The texture and cation exchange capacity (CEC) of the collected soil was checked using pipette and ammonium acetate (pH 7.0) methods, respectively. Furthermore, the soil samples were digested with $HCl:HNO_3:HClO_4$, and both metals contents were determined using atomic absorption spectrophotometer (AAS). The rice straw derived biochar (BC) (made at temperature 500°C) was bought from biochar production company Wuhan, China, while, slag (SL) and ferrous manganese ore (FMO) were collected from the Lab of Remediation Polluted Environment, College of Resources and Environment, Huazhong Agricultural University, Wuhan, China. The basic physio-chemical properties of soil and BC were as: pH 5.82 and 10.28, EC 2.3 and 1.8 mS cm^{-1}, Cd 0.04 and 0.03 mg kg^{-1}, and Pb 23 and 22 mg kg^{-1}, respectively while, soil organic matter was 2.52% and texture was silty clay loam.

For incubation, each cup of polythene was filled with 200 g soil and contaminated with $Pb(NO_3)_2$ and $Cd(NO_3)_2$ to attain the soil Pb and Cd contamination levels of 1000 and 20 mg kg^{-1} respectively, and then kept for 60 days at 70% (w/v) maintained moisture level at 25°C. After 60 days of incubation period, two levels [0.5% and 1% (w/w)] of BC, SL and FMO were amended in the contaminated soil and the soil without any amendment was tagged as controlled. The experimental design was conducted following completely randomized design (CRD) with three replicates. All the amendments were mixed thoroughly at 70% of the water holding capacity with deionised water retaining all the cups covered with a plastic lid to avoid moisture loss, and to allow gaseous exchange through small holes which were made in the lid. The samples were again incubated at 25°C for another 60 days, while after every 5 days, the cups were balanced and watered to sustain moisture level throughout the study. At the end of the experiment, further chemical analyses were done after air drying and grinding the samples. Heavy metal contents, after the incubation period, were analyzed by atomic absorption spectrophotometer (AAS) model Agilent 240FS-AA.

The European Community Bureau of Reference (BCR) progressive extraction technique was applied to examine the total metal concentration (Rauret et al. 1999) as described in detail by Jiang et al. (2012). Briefly, Step 1 (acid-soluble fraction), 0.5 g soil was extracted by shaking at 25°C having 20 ml acetic acid (0.11 mol l^{-1}) for 16 h, centrifuged, filtered and stored at 4°C for further analysis. Distilled water was used to wash the remaining soil from step 1. In step 2 (reducible fraction), the remaining soil samples from step 1 was extracted by adding 20 ml solution of hydroxylamine hydrochloride (0.1 mol l^{-1}), shaken, centrifuged, filtered and stored at 4°C in a similar way as described in step 1. In step 3 (oxidizable fraction), the residues from step 2 were twice digested in water bath with 10 ml hydrogen peroxide (8.8 mol l^{-1}), acidified to pH 2–3 and then 25 ml solution of ammonium acetate (1.0 mol l^{-1}) was used for extraction in a similar way as described in step 1. Soil residues were digested with $HCl:HNO_3:HClO_4$ acids to extract the final residual fraction. After digestion, samples were preserved at 4°C until analysis. Concentration of metals in all solutions was determined by the atomic absorption spectrophotometer (AAS) model Agilent 240FS-AA. USEPA 1311 (USEPA 1992) method was used to calculate heavy metal solubility in TCLP extractable metal concentration. Briefly, 1 g soil was poured into centrifuge tube, and 20 ml un-buffered glacial acetic acid solution (pH 2.88 ± 0.01) was added and centrifuged at 4000 rpm for 20 min after shaking on end to end shaker at 30 rpm for 18 h. Then, AAS was used to analyze the metals from filtered supernatant. While, for $CaCl_2$ and NH_4NO_3 extraction, 2 g soil was taken in 50 ml centrifuge tube along with 0.01 mol $CaCl_2$ and 1 M NH_4NO_3 respectively. Then, soil was shaken for 2 h, after shaking samples were centrifuged, filtered and stored to measure exchangeable Pb and Cd concentration by using AAS (Houben et al. 2013; Schlichting et al. 1995). Data was analyzed by using statistix 8.1v to perform analysis of variance (ANOVA) and LSD at the significant difference ($p < 0.05$).

Results and Discussion

The effects of passivators on the soil electrical conductivity (EC) and pH were examined after an incubation period in contaminated soil as illustrated in Fig. 1. Application of passivators significantly increased the soil EC. Compared to control, the addition of biochar (BC) (0.5% and 1%) to the soil resulted in two times increase in soil EC (1.2–2.4 mS cm^{-1}). The results are consistent with the study of Fellet et al. (2011) who reported that the addition of BC significantly increased the soil EC. Similarly, ferrous manganese ore (FMO) and slag (SL) also showed a slight increment in soil EC as compared to control.

Soil pH was also increased with the addition of BC such as the application of 1% BC treatment resulted in higher pH values. The application of BC was more effective than SL and FMO in increasing soil pH. Generally, BC contained base cations which transform into carbonate, oxides and hydroxides that cause alkalinity, and ultimately increases in soil pH (Houben et al. 2013). Moreover, SL also helped to increase the soil pH which might be due to the presence of several base cations and plenty of CaO, MgO and SiO_2 ions, which induce the liming effects and increase soil pH (Ning et al. 2016). After the incorporation of these amendments in the metals-contaminated soil, the soil pH was increased and ultimately led to the immobilization of heavy metals through the hydrolysis process (Lu et al. 2014), and might be precipitated as $CdCO_3$ and $Pb_5(PO_4)_3Cl$ (Mousavi et al. 2010).

Figures 2 and 3 show the effects of various amendments on geochemical fractionation of Pb and Cd: acid soluble, reducible, oxidisable and residual portion in co-contaminated soil. The application of all amendments significantly decreased the acid soluble fraction, however the addition of biochar (BC) at the rate of 0.5% and 1% prominently decreased the Pb from 46.6% to 51.3% and Cd from 21.3% to 34.73% respectively than control. These results are same in line with Shaheen et al. (2015) who reported that metal-polluted soil amended with BC exhibited the lower acid

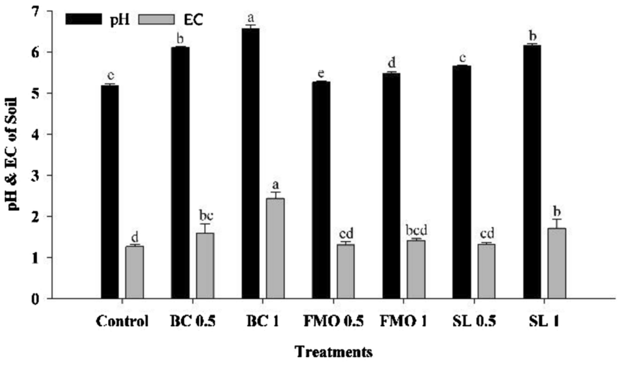

Fig. 1 Soil pH and EC (mS cm^{-1}) changes after treated with various soil amendments. Treatments: control, rice straw derived biochar (BC), slag (SL) and ferrous manganese ore (FMO). Values are means of three replicates and contain standard deviations (n = 3). Bars with different letter indicate significant differences between treatments at $p < 0.05$

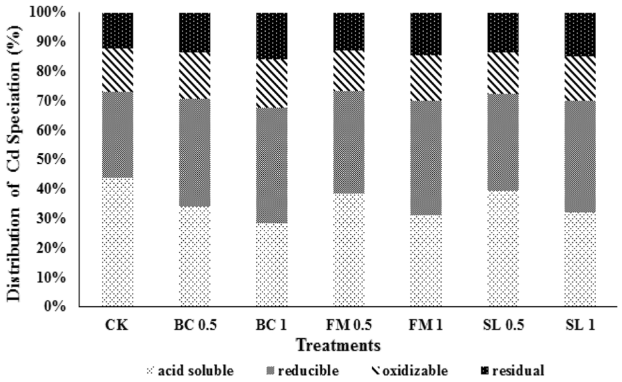

Fig. 2 Soil Cd speciation after treatments with various amendments. Treatments: Control, rice straw derived biochar (BC), slag (SL) and ferrous manganese ore (FMO). Values are means of three replicates and contain standard deviations (n = 3). Bars with different letter indicate significant differences between treatments at $p < 0.05$

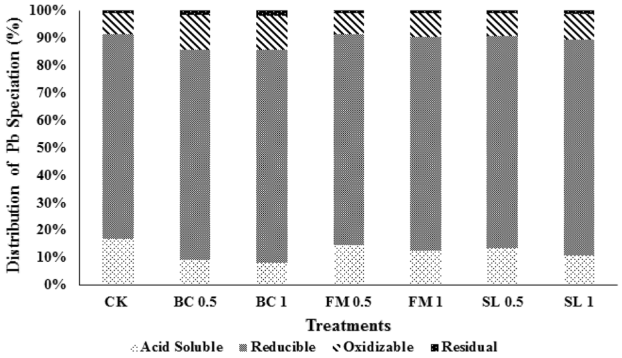

Fig. 3 Soil Pb speciation after treatments with various amendments. Treatments: Control, rice straw derived biochar (BC), slag (SL) and ferrous manganese ore (FMO). Values are means of three replicates and contain standard deviations (n = 3). Bars with different letter indicate significant differences between treatments at $p < 0.05$

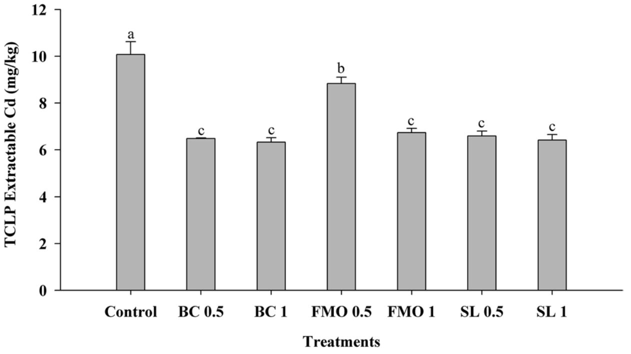

Fig. 4 The effects of amendments on the extractable Cd using TCLP. Treatments: Control, rice straw derived biochar (BC), slag (SL) and ferrous manganese ore (FMO). Values are means of three replicates and contain standard deviations (n = 3). Bars with different letter indicate significant differences between treatments at $p < 0.05$

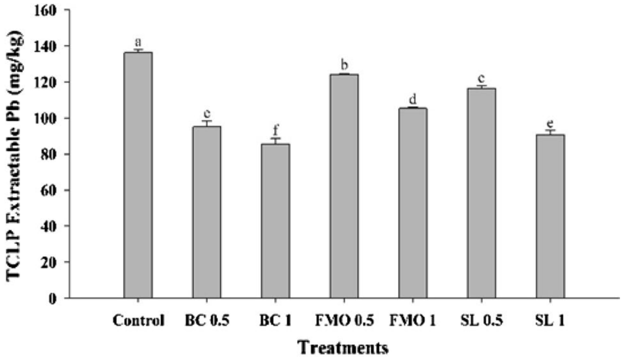

Fig. 5 The effects of amendments on the extractable Pb using TCLP. Treatments: Control, rice straw derived biochar (BC), slag (SL) and ferrous manganese ore (FMO). Values are means of three replicates and contain standard deviations (n = 3). Bars with different letter indicate significant differences between treatments at $p < 0.05$

soluble fraction of heavy metals as compared to control. It was proposed that the decrease in an acid soluble portion of Cd and Pb might be due to the higher sorption ability of BC. In addition, the application of of BC also increased the heavy metal binding with Fe, Mn and carbonates which ultimately resulted in the generation of an insoluble stable complex form of metals (Ahmad et al. 2014). While, the addition of SL at the rate of 1% also showed a reduction in acid soluble portion of Pb (about 35%) and Cd (about 28.60%) as compared to control. On the other hand, the application of FMO showed a slight reduction in acid soluble fraction for both Pb and Cd, over the untreated soil. It has also been reported that the addition of organic amendments increased the heavy metal adsorption and precipitation on the surface (Ahmad et al. 2014). The obtained findings indicate that in the soil amended with different passivators, the reducible fraction exhibited higher values of Pb and Cd than others fractions. Particularly, the addition of BC at 0.5% and 1% offered a greater amount of Pb and Cd in reducible portion as compared to SL and FMO. Similarly, the oxidisable portion of Pb and Cd was also increased by 38.4%–37.9% and 8.5%–10.6% with the incorporation of BC at 0.5% and 1%, respectively. All the amendments showed a positive increment in residual portion, while BC offered a greater increment in the residual portion of Pb and Cd as compared to SL and FMO. Whereas, the residual Cd and Pb were increased about 4.3% and 13.8%, respectively, than control with the addition of SL at the rate of 1%. All the amendments added to co-contaminated soil markedly influenced the soluble or exchangeable fractions of both metals, especially the soluble portion, whereas their concentration was increased more in reducible and oxidisable portion which might be possible due to increase in soil pH. These results are in accordance with Aboulroos et al. (2006), who confirmed that the incorporation of steel slag reduced the exchangeable Cd concentration by 100% and increased reducible fraction of Cd by 50% as compared to untreated soil. The steel slag enriched with the oxides of Ca, Fe and Mn effectively increased the metals precipitation by forming their insoluble complexes with the increase in soil pH (Liang et al. 2005). The obtained findings also revealed that the Pb concentration was mainly increased to reducible and oxidizable portions of the soil amended with SL which might be occurred due to its binding with carbonates, Fe and Mn-oxides. These results show an agreement with the previous study conducted by Ning et al. (2016). Furthermore, it was observed that increment in Pb immobilization was mainly triggered by an increase in soil pH (Shaheen et al. 2015). Overall, the maximum amount of Cd and Pb were decreased to their soluble form while the reducible and oxidisable fractions increased when contaminated soil was exposed to different amendments. These findings are in accordance with the results obtained by Saffari et al. (2015), and reported that the possible reason was the formation of amorphous Fe-oxides by the oxidizing process (Houben et al. 2012). Naidu et al. (1994) and Saffari et al. (2015) reported that application of metal oxides such as Fe and Mn-oxides enhanced the surface adsorption of Cd due to presence of OH^- groups, and Cd-proton exchanges with the surface of soil enriched with negative charges.

The results about TCLP extraction showed that the concentration of Cd and Pb were higher than their permissible level (< 5 mg L^{-1}) in the untreated soil and hence, it was dangerous to human beings as per the criteria recommended by the U.S. Environmental Protection Agency (USEPA 1992) (Figs. 4, 5). The TCLP extractable Pb and Cd were significantly ($p < 0.05$) reduced in the contaminated soil treated with BC and SL. The addition of BC at the rate of 0.5% and 1%, markedly reduced the TCLP extracted Pb from 30.1% to 37.2% and Cd from 35.6% to 37.2% as compared to control. These findings are in accordance with the results

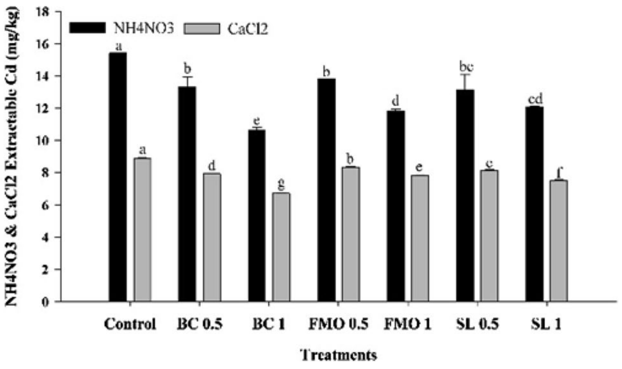

Fig. 6 The effects of amendments on NH_4NO_3 and $CaCl_2$-extractable Cd. Treatments: Control, rice straw derived biochar (BC), slag (SL) and ferrous manganese ore (FMO). Values are means of three replicates and contain standard deviations (n = 3). Bars with different letter indicate significant differences between treatments at $p < 0.05$

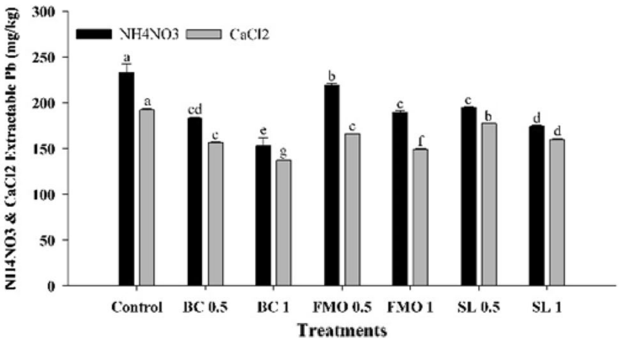

Fig. 7 The effects of amendments on NH_4NO_3 and $CaCl_2$-extractable Pb. Treatments: Control, rice straw derived biochar (BC), slag (SL) and ferrous manganese ore (FMO). Values are means of three replicates and contain standard deviations (n = 3). Bars with different letter indicate significant differences between treatments at $p < 0.05$

reported by Lu et al. (2014), who indicated that the application of BC reduced the heavy metals because of liming effects, high mineral ash contents and plenty of functional groups on its surface. Furthermore, the obtained results also indicate that the application of FMO showed less reduction in TCLP extractable Pb and Cd. Additionally, the application of SL also showed reduction in extractable Pb and Cd, nonetheless SL at the rate of 1% was proved more effective in decreasing of TCLP for Cd (36.3%) than Pb (33.3%). These findings are in contrast to the standards set by USEPA (1992).

The changes in extractable Pb and Cd by NH_4NO_3 and $CaCl_2$ in co-contaminated soil amended with different passivators is presented in Figs. 6 and 7. All the passivators exhibited a decreasing trend for soil NH_4NO_3 and $CaCl_2$-202 extractable Pb and Cd which was observed by 233.43, 15.43 and 192.25, 8.89 mg kg^{-1} respectively, realtive to the control. Compared with the untreated soil, the NH_4NO_3 and $CaCl_2$ extractable Pb and Cd were significantly reduced by 21.47%, 34.40% and 13.60%, 28.47% for Pb and 13.60%, 31.25%, and 13.60%, 24.25% for Cd when treated with 0.5% and 1% of BC, respectively. The absorption of NH_4NO_3 and $CaCl_2$-extractable Pb and Cd was also reduced with the application of SL (Figs. 6, 7). On the other hand, the application of FMO at the rate of 0.5% and 1%, the concentration of NH_4NO_3 and $CaCl_2$-extractable Pb was reduced from 5.97%–18.74% to 10.44%–23.32% and Cd was reduced from 13.55%–22.26% to 6.07%–11.93% as compared to untreated soil. Soil pH known as a major factor in metal speciation as well as to the ratio of the mobile pool to the total metals in soil (Zeng et al. 2011). The results also indicated that with the addition of BC, the solubility and leachability of Pb and Cd was reduced maximally because of adsorption and precipitation processes. These findings are same in line with the results of Ning et al. (2016). Our results also indicated that solubility and mobility of Cd and Pb decreased because of high pH, surface area and CEC of biochar and slag. In general, all types of BC and SL had microporous structures, high pH and CEC and small particle size, which provide greater surface area and higher adsorption ability. The presence of oxides, and sufficient amount of SiO_2 in SL cause alkalinity which might be the possible reason to increase soil pH, and functional groups also play a key role for heavy metal immobilization (Yuan et al. 2011; Gu et al. 2011; Chen et al. 2016). Similarly, the recent study reported by Bing et al. (2016) confirmed that the addition of SL notably reduced the metals concentration in the $CaCl_2$ extract. It can be attributed that addition of alkaline amendments and hence increase in soil pH, which triggered heavy metals precipitation and adsorption on the soil surface because of excess negative charges on the surface (Chen et al. 2016). Moreover, the results also indicated that the use of FMO also had a positive influence on the immobilization Cd and Pb in acidic soil, again the possible reason might be increase in soil pH and role of oxides present on iron and manganese surfaces. Previously also reported that zero valent iron had a strong influence on metals immobilization by reducing their solubility and also transforms the metals into oxide occluded fractions. It was also demonstrated that the addition of iron and manganese ore prominently reduced the liable pool of heavy metals through adsorption and precipitation (Watanabe et al. 2009; Ok et al. 2011). As a whole, the order tailed by the passivators on the overall reduction of Pb and Cd was following: BC > SL > FMO > Control.

Moreover, the use of applied passivators on a field scale is recommended, because a variety of passivators are being used for hindering the toxicity of heavy metals. Application of biochar (BC) in the field is a valuable practice because it has a great influence on soil physicochemical and biological properties, and can also help in the reduction of greenhouse gas emission (Rondon et al. 2005; Lehman and Joseph 2009;

Spokas et al. 2009). Commonly, BC has low particle density, because of this when it is applied in the field, it has the tendency to reduce bulk density of soil, improves structure and permeability of soils (Masulili et al. 2010; Yamato et al. 2006; Yoshizawa et al. 2007). It also helps to retain soil moisture and improves CEC, porosity, pH, nutrient bank and soil quality in relationship to carbon and energy (Warnock et al. 2007; Meng et al. 2011; Lehman et al. 2006). Similarly, ferrous and manganese ores also showed potential for accepting the electrons present in anoxic soil as oxides, hydroxides as a structure of clay mineral (Stucki 1988). Furthermore, presence of Fe in the soil also helps in the mineralization of soil organic matter and NH^{4+} release (Sahrawat 2003, 2004). Slag is a waste material of industries and can be used as a passivator against heavy metals contamination because SL contained a variety of compounds and minerals such as TiO_2, Fe_2O_3, FeO, Fe_3O_4, BaO, MgO, CaO, MnO and SiO_2 at varying amounts which make it a very good choice as adsorbents (Bing et al. 2016). It also had the tendency to increase soil pH through which oxides of Ca, Fe and Mn take part to increase metals-precipitation by forming their insoluble complexes (Liang et al. 2005). In addition, steel slag also had a greater surface area and pore space, which might be helpful to increase the immobilization of metals through adsorption on its surface (Xue et al. 2009).

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