Characteristics and Mechanisms of Heavy Metal Adsorption on Biochar and Its Application in Soil Remediation

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Abstract

Biochar is the solid carbon-rich product resulted from heating biomass (typically agriculture wastes) in an oxygen limited environment in a process called pyrolysis. Biochar production converts the labile carbon, which has been absorbed and stored by biomass typically through photosynthesis, into recalcitrant charcoal. Bio-oil and syn-gas, which are the liquid and gas co-products of biochar respectively, can be used as bioenergy. The incomplete carbonisation during production gives biochar relatively high surface area, high pH, high cation exchange capacity (CEC), high aromaticity and active functional groups. These properties result biochar in high adsorption capacity of heavy metals, which are typical contaminants in soils. They can enter the water source of humans through underground water flow or be uptaken by crops, which both will result in ingestion by humans directly or indirectly. Heavy metals can cause serious health problems to humans such as cancer, skin irritations, reproductive damage, mental health problems or death. Due to the proposed high adsorption capacity of heavy metals, biochar can immobilise them in the soil and therefore reduce their risks to the environment when applied to contaminated soils. The application of biochar to soil remediation has additional benefits including waste management, energy production and carbon storage. It is therefore important to investigate the potential of biochar application in soil remediation of heavy metals, among which a few research gaps are particularly crucial. This thesis identified these research gaps through a critical literature review and investigated them.

Salisbury biochar (derived from British broadleaf hardwood) was applied to two different contaminated soils (a field sandy made-ground contaminated soil and a laboratory artificially contaminated clay soil). The impact of Salisbury biochar on the mobility and speciation of heavy metals in the two soils were investigated. The field study showed the mobility of Ni^{2+} and Zn^{2+} in the plots with biochar addition (dosage of 0.5-2% in w/w) were much lower than those without biochar addition. Biochar is regarded to play a key role in reducing the Ni^{2+} and Zn^{2+} leachabilities of soils 36 months after the treatment. This was confirmed by sequential extraction test results which indicated that biochar addition enhances the residual fractions of Ni^{2+} (by 10-15%) and Zn^{2+} (by 20-28%) in the soils through competitive adsorption and consequently reduces their mobility. The low leachabilities of Cu^{2+} and Pb^{2+} indicate a high immobilisation of them by soil itself and a low risk to the environment, although

biochar addition still enhanced their residual fractions in the soils. The laboratory study found that Saslisbury biochar (dosage of 1% in w/w) did not have a siginificant effect on the mobility or speciation of Pb^{2+} in the kaolin during 28 days after the treatment due to a competetive adsorption by kaolin.

In order to aid the understanding of the interactions between heavy metals and biochar, two separate adsorption studies were carried out to investigate the adsorption of heavy metals to different biochars: adsorption of Pb^{2+} to Salisbury biochar, and adsorption tests of Ni^{2+} to eight standard biochars. The adsorption characteristics of Pb^{2+} on Salisbury biochar showed that biochar particle size, solid to liquid ratio and the solution pH significantly affect the adsorption of Pb^{2+} to Salisbury biochar. The calculated maximum monolayer adsorption capacities of Salisbury biochar for Pb^{2+} were 0.145-0.230 mmol/g. The adsorption characteristics of Ni^{2+} on eight standard biochars, including kinetics, the influence of solid to liquid ratio, the influence of solution pH and adsorption equilibrium, were investigated. The adsorption capacities of Ni^{2+} for six of the standard biochars (0.126-0.398 mmol/g) were higher than that of Salisbury biochar (0.105 mmol/g). Both pH and CEC of biochar can be a relatively good indicator of the adsorption capacity of heavy metals for the standard biochars through an approximately positive linear and exponential relationship respectively.

Chemical and micro-structural methods were conducted to further investigate the adsorption mechanisms of heavy metals on biochars both qualitatively and quantitatively. Sequential extraction results suggest approximately 85.31% of totally adsorbed Pb^{2+} falls in acidic soluble fraction and is potentially bioavailable. Micro-structural test results suggest that this fraction was mainly cerussite (accounted for 82.24% of the totally adsorbed amount of Pb^{2+} in Salisbury biochar at initial Pb^{2+} concentration of 5 mM (0.1 g biochar in 20 mL solution)). The environmental implications of this was further discussed together with the findings from the application of Salisbury biochar to the two contaminated soils. The sequential extraction results (the data with recoveries > 70%) suggest that the majority of heavy metals (Pb^{2+}, Cu^{2+} and Ni^{2+}) adsorbed on the selected standard biochars falls in acidic soluble fraction, which represents the heavy metals adsorbed on biochar through surface precipitation or cation-π interaction. The micro-structural tests confirm the presence of Pb^{2+} precipitates in the form of hydrocerussite and Cu^{2+} precipitates in the form of gerhardtite on some the selected standard biochars.