Influence of bioenergy waste biochar on proton- and ligand-promoted release of Pb and Cu in a shooting range soil

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HIGHLIGHTS

- Presence of protons and ligands in soil increased the bioavailability of Pb and Cu.
- Biochar reduced Pb and Cu release rates to 99.5%.
- Electrostatic attraction and complexation to biochar could immobilize Pb and Cu.

GRAPHICAL ABSTRACT
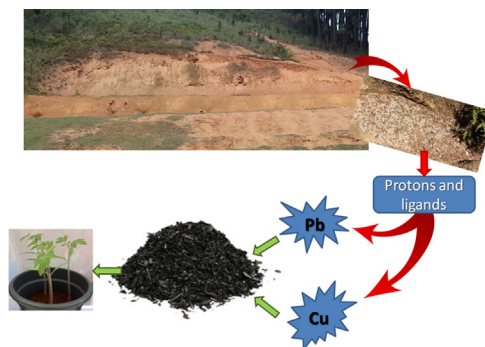
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ABSTRACT

Presence of organic and inorganic acids influences the release rates of trace metals (TMs) bound in contaminated soil systems. This study aimed to investigate the influence of bioenergy waste biochar, derived from *Gliricidia sepium* (GBC), on the proton and ligand-induced bioavailability of Pb and Cu in a shooting range soil (17,066 mg Pb and 1134 mg Cu per kg soil) in the presence of inorganic (sulfuric, nitric, and hydrochloric) and organic acids (acetic, citric, and oxalic). Release rates of Pb and Cu in the shooting range soil were determined under different acid concentrations (0.05, 0.1, 0.5, 1, 5, and 10 mM) and in the presence/absence of GBC (10% by weight of soil). The dissolution rates of Pb and Cu increased with increasing acid concentrations. Lead was preferentially released (2.79×10^{-13} to 8.86×10^{-13} mol m^{-2} s^{-1}) than Cu (1.07×10^{-13} to 1.02×10^{-13} mol m^{-2} s^{-1}) which could be due to the excessive Pb concentrations in soil. However, the addition of

GBC to soil reduced Pb and Cu dissolution rates to a greater extent of 10.0 to 99.5% and 15.6 to 99.5%, respectively, under various acid concentrations. The increased pH in the medium and different adsorption mechanisms, including electrostatic attractions, surface diffusion, ion exchange, precipitation, and complexation could immobilize Pb and Cu released by the proton and ligands in GBC amended soil. Overall, GBC could be utilized as an effective soil amendment to immobilize Pb and Cu in shooting range soil even under the influence of soil acidity.
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1. Introduction

Contamination of soil by heavy metals through geogenic and anthropogenic inputs is considered to be a global problem. The dissolution of heavy metals-bearing minerals is an important aspect of environmental contamination (Feng et al., 2017a, 2017b; Lin and Valentine, 2008). Anthropogenic activities including mining operations and industrial discharge may enhance the heavy metals mobilization in the natural environment (Roussel et al., 2000; Yun et al., 2016). In recent years, military shooting ranges have been identified as a possible anthropogenic source for increasing the levels, mobility, and bioavailability of heavy metals in the environment. Shooting range soil consists of elevated concentrations of metal(loid)s such as Pb, Cu, Zn, Ni, Sb and As, released from used bullets and bullet fragments (Ahmad et al., 2012a; Moon et al., 2013). Shooting range soils are usually less fertile and non-arable due to nutrient deficiency (Liyanage et al., 2016). Different chemical processes, including oxidation, carbonation, and hydration may dissolve metals from the bullets, leading to elevated soluble metal concentrations in soil (Ma et al., 2007). In many cases, shooting range soils exceed the total Pb concentration of 10,000 mg kg^{-1} (Bannon et al., 2009; Sehube et al., 2017). These Pb levels are often 25 fold greater than United States Environmental Protection Agency (USEPA) screening criteria for Pb, i.e., 400 mg kg^{-1} (USEPA, 1996).

Soil acidity is a common issue related to various environmental and human activities such as acid deposition, acidic parent material, organic matter decomposition, rhizospheric activities, etc.. The release of TMs from the soil, sediments, rocks and minerals with respect to time and land use is governed by different variables such as type and concentration of available acids, solution pH, protons, ligands and ionic strength in the solution. Increase in soil acidity at a shooting range can significantly increase the mobility of existing TMs. It has been observed that the presence of protons and ligands enhance the metal complexation and release. The effect of three organic acids (with mono, di and tri carboxylic groups) and inorganic acids (different protonation capacities) may influence the trace metal mobilization and remediation ability of biochar (Kumarathilaka et al., 2016; Rajapaksha et al., 2012). Acidic conditions in shooting soil enhance the breakdown of bullet pellets, thereby increasing the mobility of metals (Cao et al., 2003). Acid deposition on soil from the atmosphere in either wet or dry form can significantly increase the mobility of metals as a result of a decrease in soil pH which is caused by the formation of inorganic acids (particularly sulfuric acid and nitric acid) (Zhang et al., 2012). Moreover, root exudation, microbial secretions and humus decomposition in the soil can also make the soils more acidic due to the production of organic acids (such as acetic acid, citric acid, and oxalic acid) (Yang et al., 2006). Consequently, deleterious effects of contaminated shooting range soils, such as groundwater and surface water pollution, reduction of the soil enzymatic activities and accumulation of TMs in animal and plant tissues, will be pronounced. Once in the soil, bullets and bullet fragments in shooting range soils steadily oxidize possibly due to the weathering actions of water, air, microbial activity as well as organic and inorganic acids. Therefore, it is important to evaluate the fate of TMs at shooting range soil under the influence of inorganic and organic acids, representing the effects of acid deposition and soil natural decomposition of organic compounds, respectively as the understanding is lacking.

Several techniques such as organic/inorganic materials (in pristine, modified, and nanoscale forms), inoculation of microorganisms, and hyperaccumulating plant species have been applied to minimize mobility and bioavailability of heavy metals in contaminated soils. (Ahmad et al., 2012b; Wen et al., 2016). There are many mechanisms could be responsible for heavy metals immobilization via adsorption, precipitation, surface complexation, ion exchange, and oxidation/reduction (Kumarathilaka and Vithanage, 2017; Ok et al., 2007; Zhang et al., 2015). Each and every technique has limitation possibly because of removal efficiency and economic feasibility. In recent years, natural or waste materials have gained significant attention due to their cost-effectiveness in terms of TMs immobilization. In this context, biochar (BC) is recognized to be an effective adsorbent for TMs immobilization (Ahmad et al., 2014; Bandara et al., 2016; Herath et al., 2015; Igalavithana et al., 2017).

Biochar is produced through the thermochemical process (pyrolysis) of biomass under oxygen-limited conditions (Guo et al., 2016; Ok et al., 2015; Sun et al., 2014). Different types of biomass (i.e., forestry and agricultural crop residues, invasive plant species, wood waste, animal manures and organic portion of municipal solid waste) can be used as feedstock to produce BC (Jayawardhana et al., 2016; Rajapaksha et al., 2015; Yuan et al., 2011). The properties of BC is highly depended on the feedstock type, pyrolysis conditions (pyrolysis temperature, heating rate, and holding time), and surface modifications (Mašek et al., 2013; Zhao et al., 2013). Application of BC to soil system has shown a significant importance because of its capability not only to improve soil nutrient content and water holding capacity but also carbon sequestration aspects to minimizing greenhouse gas emissions (Novak et al., 2012; Zhang et al., 2012). Simultaneously, BC has proven its potential role for organic contaminants (i.e., pesticides and antibiotics) removal in soil and water systems (Vithanage et al., 2015, 2016).

Protons and ligands can act as chelating agents and influence the release of TMs in such soils (Rajapaksha et al., 2012). Although the effects of BC on TMs immobilization in the soil are studied in detail, sufficient attention has not been given for assessing its influence on organic and inorganic acids for the release/immobilization rates of TMs in multimetal contaminated soil systems (Rajapaksha et al., 2012). Hence, the purposes of the present study were to: (1) assess the fate of Pb and Cu in a shooting range soil influenced by protons (sulfuric, nitric and hydrochloric) and ligands (citric, oxalic and acetic), (2) evaluate the effectiveness of the BC produced from *Gliricidia sepium* biomass for the immobilization of Pb and Cu under soil acidic conditions, and (3) propose possible interactions of BC with Pb and Cu in the presence of different organic and inorganic acids.

2. Materials and methods

2.1. Soil collection and characterization

A shooting range soil, obtained from a military academy of the Uva Province, Sri Lanka, was used for this study as a model soil. The soil was dug out to a depth of 15 cm and collected in sealable polyethylene bags. Six subsamples were randomly collected across the field. After sent to the laboratory, a composite sample was prepared by mixing each subsample. Then the soil sample was air-dried and mechanically sieved to <2 mm fraction. The pH and electrical conductivity (EC) of the soil were measured in 1:10 suspensions of soil-to-water using the digital pH meter (702SM Titrino, Metrohm) and electrical conductivity meter (Orion 5 star meter, Thermo Scientific). Total organic carbon

(TOC) was determined by using wet oxidation by acidified dichromate method described by Anderson and Ingram (1998). In addition, shooting range soil was evaluated via X-ray diffraction (XRD) using Shimadzu XRD-700 diffractometer (Japan) operating with 30 mA Cu Kα radiation in a continuous scan mode. X-ray diffraction patterns were collected between 2θ values of 10.0–60.0° at a scan speed of 2° min^{-1}. The texture of the shooting range soil was determined by particle size analyzer (Mastersizer 2000) after mixing the soil with Calgon reagent mixture (Na_2CO_3 and $NaPO_3)_6$). Specific surface area of the shooting range soil was determined via methylene blue test (Yukselen and Kaya, 2008).

A microwave digester (MARS 5, CEM Corporation) was used for soil sample digestion. Soil samples were digested according to a modified EPA method 3051 to determine the total concentration of elements. Acid-cleaned Mars express digestion vessels were used and 0.2 g of soil sample was measured into the vessels with 4 and 3 mL of concentrated HNO_3 and HCl acids, respectively. The digestion method consisted of a 5 min ramp to 175 °C, with a 20 min hold before cool down. All digested samples were rinsed from digestion vessels to 25 mL volumetric flask and filtered through Whatman 42 filter paper after dilution to 25 mL using Millipore water (18.2 MΩ cm). Diethylene triaminepentaacetic acid (DTPA) extraction developed by Lindsay and Norvell (1978) was performed to evaluate the extractable metals in shooting range soil. Approximately 20 mL of a DTPA, 0.01 M $CaCl_2$ and 0.1 M triethanolamine-buffered solutions were added to 10 g of shooting range soil. The solid solution was stirred for 2 h. Thereafter, soil solution was centrifuged at 3500 rpm for 10 min (ROTANTA 460) and filtered. All digested and extracted samples were analyzed for Pb, Cu, Sb, As, Zn, Ni, Cr and V by using inductively coupled plasma optical emission spectrometer (ICP-OES; Optima 4300 DV, PerkinElmer, USA). Multi-element standard solution (Quality Control Standard 21, PerkinElmer) was used to make calibration standards for ICP-OES. Calibration curves were set up and ensured that the residual mean square (R^2) was greater than or equal to 0.99. The quality assurance and quality control (QA and QC) of the analysis were conducted for sample blank (Millipore water), instrument calibration standard (1 mg L^{-1} of Mn) and full calibration check per 25 samples.

2.2. Biochar production and characterization

Biochar, produced as a byproduct from a bioenergy industry at Thirappane, north central province, Sri Lanka via gasification of *Gliricidia sepium* biomass, was obtained. The reactor temperature of this process is maintained at 900 °C and the limited air is used for the gasification. The obtained BC was air dried and ground to <1 mm before use. The pH and EC were measured in 1:5 suspensions of BC-to-water using the digital pH meter and electrical conductivity meter, respectively. Proximate analysis was conducted based on the experimental procedure given in Ahmad et al. (2013) and elemental compositions were determined by the elemental analyzer (EuroEA Elemental Analyzer). Morphology of GBC was characterized by scanning electron microscopy (SEM) (FEI Inspect S50). Furthermore, BET surface area and pore volume of the *Gliricidia sepium* BC (GBC) was obtained from our previous study (Kumarathilaka and Vithanage, 2017).

2.3. Pb and Cu release with inorganic and organic acid extractions

Three inorganic (sulfuric, nitric and hydrochloric) and Three organic (acetic, citric and oxalic) acids of different concentrations (i.e., 0.05, 0.1, 0.5, 1.0, 5.0 and 10 mM) were used to evaluate the proton and ligand influence as chelating agents for Pb and Cu release in the shooting range soil. This concentration gradient was selected to represent the extreme environmental changes possibly over time and studies with same concentration gradient have been reported in literature as well (Rajapaksha et al., 2012). Shooting range soil (50 g L^{-1}) was placed in polypropylene tubes and 10 wt% of GBC and 20 mL of each acid with different concentrations were added. Based on the previous literature and

considering no production cost involved, we have set the GBC supplementation rate as 10% (Moon et al., 2013). Afterwards, tubes were equilibrated for 24 h at room temperature (~26 °C) and agitated on an orbital shaker at 100 rpm. The supernatant was filtered through Whatman 42 filter paper after centrifugation at 3500 rpm for 10 min. The filtered solutions were analyzed for pH, and Pb and Cu concentrations by using the ICP-OES. Each treatment was performed in triplicate.

Lead and Cu release rates were studied with respect to each acid concentration (i.e., sulfuric, nitric, hydrochloric, acetic, citric and oxalic) to determine the extent of both proton and ligand promoted metal release with the presence and absence of GBC. This dependence can be expressed in the following form (Eq. (1)) (Hamer et al., 2003; Kumarathilaka et al., 2016)

$$R_T = k_T a_{acid}^{n_T} \tag{1}$$

where R_T is the rate of release, k_T is the empirical rate constant for total metal released due to each acid, n_T corresponded to experimentally determined factor, and a_{acid} is the concentration of each acid.

2.4. Statistical analysis

Statistical analysis was performed to identify any possible correlation between medium pH and the Cu and Pb release rates. The Pearson correlation coefficient was used to measure the strength of linear associations and SAS statistical software package (SAS 9.1) performed all the statistical analysis.

3. Results and discussion

3.1. Soil characterization

Fig. 1(a) shows the mineralogical composition of the shooting range soil. Mineralogy of the soil sample was mainly comprised by quartz (SiO_2) followed by kaolinite [$Al_2Si_2O_5(OH)_4$] and muscovite [$KAl_2(AlSi_3)O_{10}(OH,F)_2$] minerals. Table 1 presents the physiochemical properties of the soil. The soil is slightly acidic with pH of 6.9. Soil texture was silty loam with the majority (67%) of silt and 7.8% clay. These values are within the range of reported values in various studies (Ahmad et al., 2012b; Lee et al., 2011), however, soil mineralogy and texture are more or less same or differ possibly because of different underlying mineralogy. Total TMs concentrations are important to use as a reference to assess intervention limit as well as to determine the contamination levels and the associated possible environmental risks (Kierczak et al., 2008). Elevated concentrations of metals such as Pb (17,066 mg kg^{-1}) and Cu (1134 mg kg^{-1}) were observed in the studied soil. Ahmad et al. (2012b) also reported that shooting range was heavily contaminated with Pb (4626 mg kg^{-1}) and moderately contaminated with Cu (225 mg kg^{-1}). Total Pb concentration (17,066 mg kg^{-1}) in the shooting range soil was approximately 57 times greater than the European Union limit for safe agricultural soil (i.e., 300 mg kg^{-1}) (Nagajyoti et al., 2010). Similarly, total Cu concentration (1134 mg kg^{-1}) in shooting range soil was nearly eight-fold greater than that of the European Union limit (i.e.,140 mg kg^{-1}) for safe agricultural soil (Nagajyoti et al., 2010). Moreover, DTPA extractable fractions of metals revealed that 4.53 and 3.35% of total Pb and Cu, respectively, were potentially bioavailable, thus presenting ecological risks.

3.2. Characterization of Gliricidia sepium BC

The SEM image (Fig. 1(b)) shows that GBC has well-developed pore structure after the pyrolysis process. Table 2 summarizes the characteristics of the GBC. The data shows that fixed carbon content (61.3%) of GBC is higher than that of mobile matter (11.0%), indicating loss of volatile matter during the thermal decomposition of *Gliricidia sepium* biomass. It is obvious that mobile and fixed carbon in BCs are prevailing
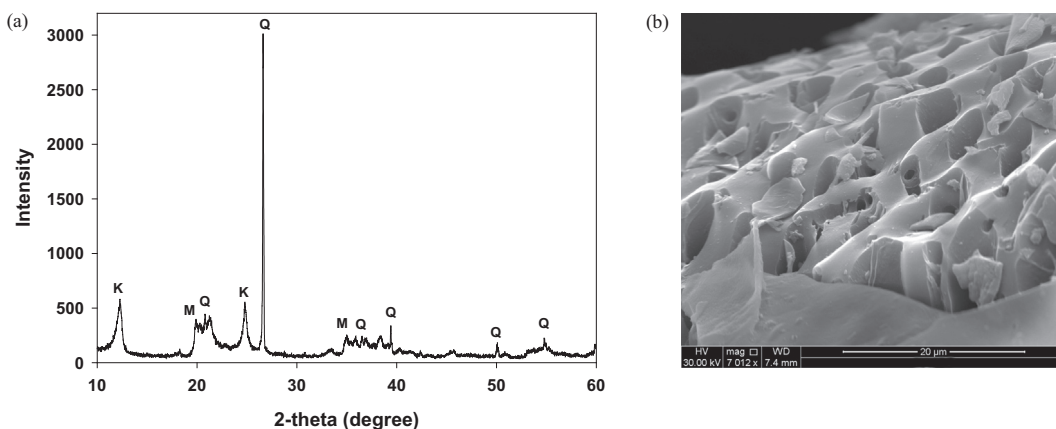
Fig. 1. (a) X-ray diffractogram of shooting range soil. (K: kaolinite, M: muscovite, Q: quartz) (b) SEM image of GBC.

factors in terms of short and long-term availabilities of carbon in the soil system. Considerably high ash content (20.6%) revealed the accumulation of inorganic minerals and organic matter combustion residues in GBC. The large BET surface area of GBC ($714 \, m^2 \, g^{-1}$) could correspond to the developments of pore structures. Relatively low H/C (0.29) and O/C (0.74) ratios are possibly due to the dehydration, decarboxylation, and decarbonylation of *Gliricidia sepium* biomass. More precisely, atomic H/C and O/C ratios are an index of aromaticity and carbonization. Even though, BC properties are significantly varied with feedstocks and pyrolysis conditions, GBC was in the range of reported values to be applied as an immobilizing agent for remediation metals-contaminated soils.

3.3. Pb and Cu release with inorganic and organic acid extractions

The rates of release for Pb and Cu increased with increasing acid concentrations in all cases (Fig. 2). The ratio between the extracted amount and the total metal concentration (Kd) (Table 3) further demonstrated that at higher acid concentrations, both Pb and Cu can favorably be released than the release at lower acid concentrations. The change in the rate of release at lower acid concentrations is much lower as compared to the change in the rate of release at higher acid concentrations. It is noteworthy that pH of the medium decreased remarkably at the acid concentrations ranged from 0.05 to 10 mM (Fig. 3). The addition of all inorganic acids decreased the pH of the medium as follows: sulfuric (from 5.74 to 3.59); nitric (from 5.98 to 4.52) and hydrochloric (from 5.96 to 3.53) and the corresponding figure for organic acids as follows: acetic (from 5.37 to 4.80); citric (from 5.59 to 2.91) and oxalic (from 4.99 to 2.76).

In comparison, Pb dissolved remarkably higher than Cu in the presence of organic and inorganic acids except for oxalic acid. This could be related to relatively high concentrations of Pb than Cu in the soil and

metal ion characteristics which determine soil's affinity for the metal. The highest release rate for Pb (8.86×10^{-12} mol m^{-2} s^{-1}) was observed in nitric acid whereas the corresponding figure for Cu (1.02×10^{-12} mol m^{-2} s^{-1}) was recorded in oxalic acids. In summary, Pb release rates increased in the order of oxalic < sulfuric < hydrochloric < citric < acetic < nitric while Cu release rates have risen in the order of acetic < sulfuric < nitric < hydrochloric < citric < oxalic. The high release rate of Pb in nitric acid treatment could be attributed to the prevalence of highly soluble $Pb(NO_3)_2$. In contrast, the relatively lower release of Pb in the presence of a sulfuric acid may be due to the precipitation of Pb as $PbSO_4$. The main reason for the weak dissolution of Pb in the presence of oxalic acid is likely to be attributed to the formation of a relatively stable Pb-oxalate precipitate ($Ksp = 2.74 \times 10^{-11}$) (reaction (2)).

$$Pb^{2+}_{(aq)} + 2C_2O^{2-}_{4(aq)} \Longleftrightarrow Pb(C_2O_4)^{2-}_{(s)} \tag{2}$$

Similarly, Cu can easily react with oxalate ion forming a stable complex of Cu-oxalate (reaction (3)) which has an extremely low solubility ($Ksp = 4.43 \times 10^{-10}$) and the stability constants of Cu-oxalate (log K = 9.2–10.3) is higher than that of Cu-citrate (log K = 4.8–5.0). However, in the presence of excess oxalate ions, the Cu-oxalate can be soluble due to the formation of high amounts of the complex, thereby making the backward reaction more dominated (McAuley and Nancollas, 1960). This may be the reason for showing an increased dissolved quantity of Cu with oxalic acid.

$$Cu^{2+}_{(aq)} + 2C_2O^{2-}_{4(aq)} \Longleftrightarrow Cu(C_2O_4)^{2-}_{(s)} \tag{3}$$

Table 1
Physico-chemical properties of shooting range soil.

Soil properties								
pH	6.90 ± 0.07							
EC (dS m^{-1})	0.10 ± 0.03							
TOC (mg kg^{-1})	5.23 ± 0.86							
Sand (%)	25.2 ± 0.56							
Silt (%)	67 ± 2.12							
Clay (%)	7.8 ± 1.55							
Surface area ($m^2 \, g^{-1}$)	72.16							
Elemental concentrations (mg kg^{-1})	Pb	Cu	Sb	As	Zn	Ni	Cr	V
Total metal	$17,066 \pm 122$	1134 ± 13.9	31 ± 1.88	1 ± 0.23	115 ± 0.09	32 ± 1.27	72 ± 7.45	130 ± 5.27
European standards for total metals to be in agricultural soils[a]	300	140	5	20	300	75	150	–
DTPA extractable metal	773 ± 14.6	38 ± 3.85	ND	0.2 ± 0.04	3.6 ± 0.57	0.1 ± 0.02	ND	ND

ND – not detectable.
[a] From Nagajyoti et al. (2010).

Table 2
Proximate composition, elemental compositions and surface area of the GBC.

Parameter	Value
pH[a]	9.72
EC (μS cm^{-1})[a]	174.9
Proximate analysis (wt%)[a]	
Moisture	7.1
Mobile matter	11.0
Ash content	20.6
Fixed carbon	61.3
Ultimate analysis (wt%)	
C	49.2
H	1.2
N	0.6
O	49.0
Molar ratio	
H/C	0.29
O/C	0.74
BET surface area (m^2 g^{-1})[a]	714
Pore volume (m^3 g^{-1})[a]	0.89

[a] (Kumarathilaka and Vithanage, 2017).

Small concentrations of organic acids added to soil system are likely to be adsorbed by organic and inorganic components in the soil, hence, negative charge or cation exchange capacity of the soil may increase. In addition, metal ions (Pb^{2+} and Cu^{2+}) in desorption solution might be bound by organic ligands attached to the soil surface (Yang et al., 2006). For this reason, low organic acid concentrations showed considerably low metals release rates. Nevertheless, the ratio of organic ligand concentration in solution to the organic ligand adsorbed by soil tends to increase with the increase in organic acid concentrations. Therefore, the increased competitive ability of organic ligands for adsorbing sites with metal ions leads to promote metal release rates. Moreover, the increment of solution pH leads to a rapid increase in net negative surface charge, as a result, soil's affinity for metal ions tends to decrease.

Interestingly, the addition of GBC decreased the Pb and Cu dissolution rates to a greater extent compared to samples that have no GBC. In the presence of all inorganic acids, reduction percentage for Pb and Cu dissolution rates ranged from 94.5–99.5 and 88.3–99.6, respectively.
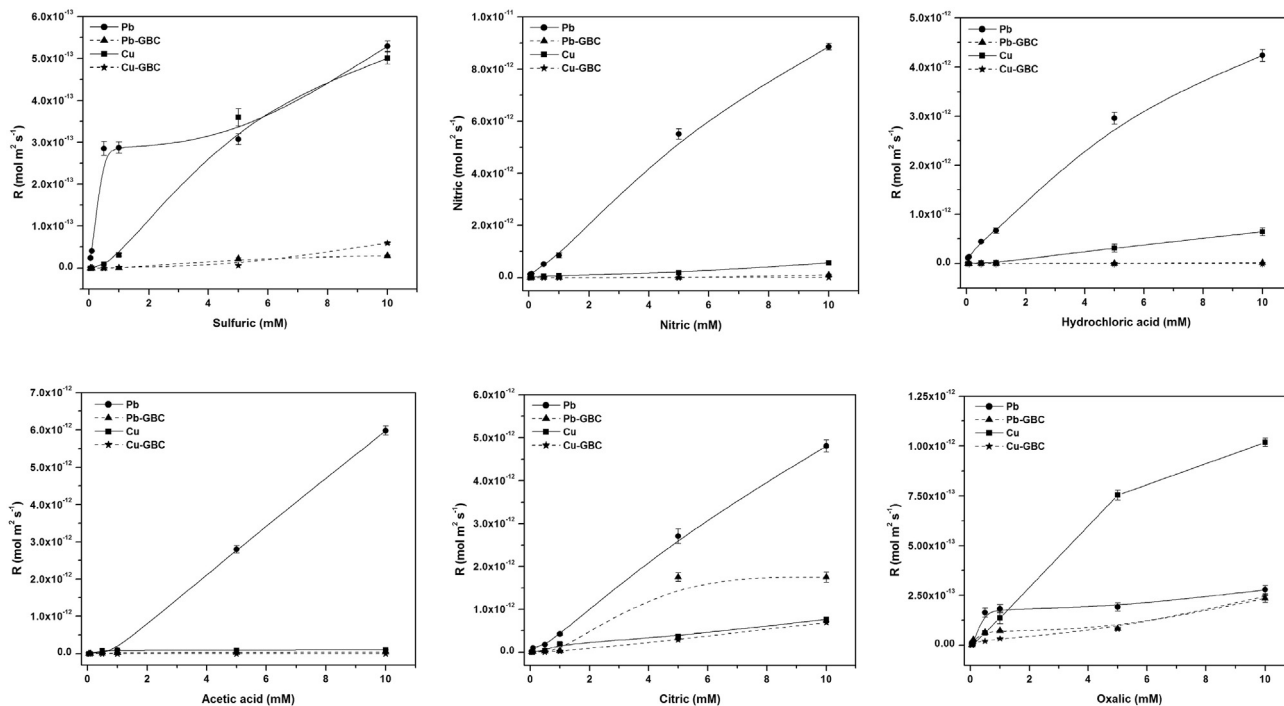
Table 3
The ratio between the extracted and total metal concentration (Kd) in each acid from 0.05 to 10 mM and with and without GBC.

Acid	Cu		Pb	
	Without GBC	With GBC	Without GBC	With GBC
Sulfuric	0.00–0.15	0.00–0.02	0.00–0.04	0.00–0.00
Nitric	0.00–0.17	0.00–0.00	0.01–0.67	0.00–0.01
Hydrochloric	0.00–0.19	0.00–0.00	0.01–0.32	0.00–0.00
Acetic	0.00–0.03	0.00–0.00	0.00–0.45	0.00–0.00
Citric	0.00–0.13	0.00–0.21	0.00–0.36	0.00–0.23
Oxalic	0.00–0.31	0.00–0.20	0.00–0.02	0.00–0.02

Similarly, reduction percentage of Pb (15.6–99.3) and Cu (10.0–99.2) in the presence of all organic acids were achieved to the same extent, despite the wide range (Fig. 2). The gained Kd values also revealed that GBC has remarkably reduced the Pb and Cu release (Table 3). Therefore, these results indicated that GBC possesses a great potential of Pb and Cu immobilization in the studied soil influenced by high soil acidity. Fig. 3 illustrates the pH variations in the medium with and without the addition of GBC in all acid concentrations. Medium pH increased to a large extent with GBC addition. For instance, with the presence of GBC, pH was increased ranging from 0.9 to 2.8 units in all selected inorganic acids concentrations whereas the corresponding figure ranged between 1.7 and 3.5 units for all selected organic acids concentrations. However, medium pH declined slightly when increasing all acid concentrations in shooting range soil.

3.4. Possible mechanisms to immobilize Pb and Cu

The primary possible explanation for Pb and Cu immobilization could be due to the alkaline nature of GBC (pH 9.72) which increase the soil pH. The correlation study indicated that the pH of the medium and Pb or Cu release rates have a strong negative correlation with or without the addition of GBC in all acids concentrations (Table 4). The pH is the measure of hydrogen ion activity and significantly influences the metals mobility. Hydrogen ions carry a single positive charge and can participate in many reactions (i.e., precipitation and dissolution of metals and redox reactions) (Stumm, 1992). Typically, in low pH

Fig. 2. Metal release rates for Pb and Cu as a function of acid concentrations and presence and absence of GBC.
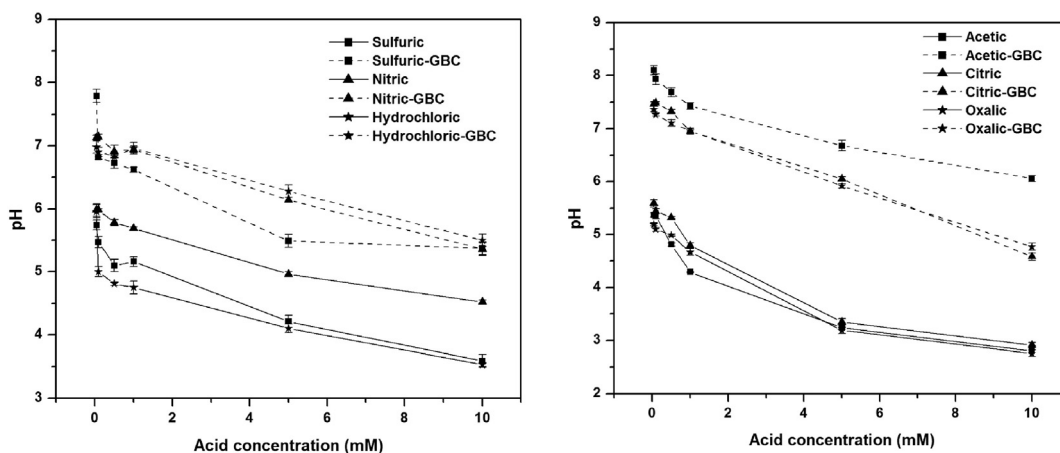
Fig. 3. Variation of medium pH as a function of different acid concentrations and presence and absence of GBC.

(high concentration of hydrogen ions), metal solubility increases since hydrogen ions compete with other positively charged ions onto the minerals or soils available sites. Contrarily, in high pH (high concentration of hydroxide ions), most metals become less mobile, possibly due to the precipitation and complexation with negatively charged hydro(oxides) (Aldriano, 2001). The increased pH may lead to deprotonation of pH-dependent cation exchange sites on soil surfaces and consequently, Pb and Cu sorption may increase.

The GBC may also stabilize Pb and Cu in shooting range soil through other sorption mechanisms including organometallic interactions, sorption due to π electron donor-acceptor interaction, pore diffusion, ion exchange and formation of stable chelates and complexes (Ahmad et al., 2014; Jiang et al., 2012; Rodríguez-Vila et al., 2015). Being transition metals, Pb and Cu tend to have good coordination affinity to bond with oxygen functional groups such as COH, C=O and –COOH of GBC surface. The presence of such O-containing functional groups on GBC surface is already confirmed in our previous study (Herath et al., 2015). The role of O-containing functional groups in BC towards metals stabilization has recently been reported by Uchimiya et al. (2011). The O atoms of these functional groups are in a position to donating their lone pair electrons to electron deficient metal centres and subsequently, organometallic interactions are formed. Further, the BCs produced at elevated temperatures exhibits high aromaticity from which metals could be sorbed through π electron donor-acceptor interactions. In other words, aromatic carbon contains double and triple bonds with a pool of π electrons which enhance π electron donor-acceptor interactions in order to sorb Pb and Cu. Since GBC reveal a high ash content (20.6%), ion exchange may be another possible mechanism to immobilize Pb. The GBC may release inorganic species such as carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), and hydroxide (OH^-) into the soil-water system, resulting in Pb immobilization through the precipitate(s) formation including $PbCO_3$, $Pb(OH)_2$ and $Pb(CO_3)_2(OH)_2$ (Ahmad et al., 2012b; Feng et al., 2017a; Sizmur et al., 2016).

Physical characteristics (i.e., surface area and pore volume) of GBC may also promote surface diffusion of Pb and Cu into the GBC. Dissolved organic carbon (DOC) concentration in soil would play an important role in mobility of Cu which forms the strongest complex with DOC than other divalent cations (Kunhikrishnan et al., 2013). More precisely, Cu mobility in soil is mainly governed by DOC concentrations despite the pH of the medium, particularly between 6.5 and 8.0. Ahmad et al. (2012b) found that the application of lime-based waste materials into the shooting range soil enhanced the Cu mobility, mainly due to the formation of Cu-DOC complexes. Contrasting results have also been reported by Lu et al. (2017) who observed that applying rice straw BC alleviated the Cu mobility in heavy metal contaminated soils. Therefore, it can be suggested that GBC addition may decrease the DOC concentration in soil and might lead to Cu sorption onto the GBC.

Therefore, the surface properties of GBC influence the Pb and Cu mobility in the shooting range soil. Biochar is a heterogeneous material comprising of several unique characteristics such as high surface area, micro-porosity, aromaticity, hydrophobicity, functional chemistry, and charged surface. Hence, different mechanisms may involve directly or indirectly in determining the interaction of metals with BC.

3.5. Integrated pollution prevention and control

Trace metal contamination of soil is considered as a widespread global dilemma and among many different techniques, phytoremediation is supposed to an efficient and cost-effective option revealing a high public acceptance due to its environmental friendliness. The key factors behind a successful phytoremediation include high phytoavailable portions of TMs in the soil solution phase, which is often not the case (Antoniadis et al., 2017; Shahid et al., 2014). However, in order to compensate, an alternative approach is the use of chelating agents which increase the uptake and translocation of TMs towards shoot tissues. Among the different chelating ligands, ethylene diamine tetraacetic acid (EDTA) is

Table 4
Correlation coefficient (r^2) and p value for Cu and Pb release rates at different pH ranges with and without GBC.

Acid	Without GBC				With GBC			
	Cu		Pb		Cu		Pb	
	r^2	p	r^2	p	r^2	p	r^2	p
Sulfuric	−0.9279	0.01	−0.8976	0.15	−0.6636	0.15	−0.8807	0.02
Nitric	−0.9352	0.06	−0.9914	0.00	−0.8911	0.02	−0.8640	0.03
Hydrochloric	−0.8500	0.03	−0.8871	0.02	−0.9064	0.01	−0.9477	0.00
Acetic	−0.8499	0.03	−0.8982	0.02	−0.9083	0.01	−0.9679	0.00
Citric	−0.9503	0.00	−0.9624	0.00	−0.9891	0.00	−0.9003	0.01
Oxalic	−0.9963	0.00	−0.8056	0.05	−0.9721	0.00	−0.9390	0.01

considered to be the most effective and efficient organic ligand in solubilizing soil-bound metals, however, is trace and enhances field leaching of metals. Hence, this study designated non-trace inorganic and organic acids to enhance the metal ion release into the soil solution. The results demonstrated that the least concentrations of the inorganic and organic acids tested in the study are suitable for inducing the release of TMs into the soil solution in an effective manner and hence, can be used for phytoremediation instead of trace ligands. Phytomining technique, which ultimately concentrates the dispersed TMs into a small volume of ash, will be a possible method to be used in terms of restoration of the shooting range soil. At the same time, BC is well capable of in-situ immobilization of TMs. Application of acids will reduce the time taken for the treatment by BC alone.

4. Conclusions

The shooting range soil was heavily contaminated with Pb and moderately contaminated with Cu. The addition of organic and inorganic acids at different concentrations leads to an increase in Pb and Cu release rates in shooting range soil due to proton- and ligand-promoted reactions. The net effect on Pb and Cu release was probably governed by the relative binding strength between metals and the soil binding sites and the complex reactions between metals and inorganic/organic acids. The application of GBC as a soil amendment played an important role in Pb and Cu immobilization. The increased pH in the medium and different physico-chemical mechanisms (i.e., electrostatic attractions, surface diffusion, ion exchange, precipitation, and complexation) could govern the immobility of Pb and Cu. Taking into account, GBC could be proposed as a potential soil amendment for shooting range soil that has been subjected to acid deposition or under natural acidic conditions promulgated by root exudates or humus decomposition, and anthropogenic activities. Since BC binds the metals via chemisorption most prominently and BC does not degrade in a human lifetime, the TMs are not available for the plants, which indicate the promising capacity of BC in in-situ immobilization of TMs in contaminated soils.

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