Composite Biochar Derived from Palm Kernel Shells and Blood Cockle Shells for Immobilizing Lead in Shooting Range Soil

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Conventionally, ground magnesium limestone (GML) has been used to immobilize lead (Pb) in soil. However, the use of non-renewable sources and the quarrying of GML may cause environmental damage. In this study, composite biochar (CPB) was prepared by pyrolyzing homogenized mixture of palm kernel shells (PKS) and blood cockle shells (BCS) at various PKS-to-BCS weight ratios, peak pyrolysis temperatures, and heating durations. Characterization of CPB was conducted using x-ray fluorescence (XRF), x-ray diffraction (XRD) spectroscopy, pH meter, and thermogravimetric analyzer (TGA). The pH values of CPB increased with decreasing PKS-to-BCS ratio and increasing peak temperature and heating duration. The pH values were measured on shooting range soil incubated with CPB9 at 1, 3, and 5% w/w. Remediation of CPB resulted an increase of pH value in the shooting range soil. Increasing content of BCS increased the pH of CPB, and decreased the solubility and mobility of soil Pb, thereby enhancing the immobilization effect of Pb in soil. These results indicated that CPB was effective in immobilizing Pb in shooting range soil due to the increasing of soil pH (9.1 to 12.0) after incubation, and reduced the exchangeable fraction (7.56% to 0.01% in CPB-treated soil) and carbonate fraction (0.51% to 0.15% in CPB-treated soil).

Key words: Composite biochar; metal immobilization; heavy metal; liming; soil remediation

Heavy metal contamination, in particular Pb, in shooting range soil is a serious problem due to its potential threats to humans. A major exposure route of Pb in soil could be by direct ingestion or inhalation of Pb dust [1]. Over exposure of Pb even at a low concentration (i.e. $10\mu g/dl$) may cause damages to the brain and nervous system, causing headaches, slowed growth, hearing problems, and impairment of vision [2]. Moreover, the impact of Pb toxicity is more severe to infants and young children than adults. The weathering of bullets in shooting range soil may be a point source of Pb contamination in water resources. Metallic Pb is transformed into ionic Pb and is more soluble and toxic to humans [3]. Shooting range soil at Sungai Besi Army Camp, Malaysia has a soil Pb content of up to 17 278 mg/kg [4]. Therefore, an immediate action is required to reduce the migration of Pb from the shooting range soil and minimize the risk of contamination to water resources. Theoretically, the decreasing of pH will increase the solubility of ionic Pb^{2+} [5].

Stabilization/solidification agents such as ground magnesium limestone (GML) is conventionally used to reduce the mobility of Pb in soil by neutralizing the acidic soil [6]. However, this approach is costly and may lead to depletion of GML. Application of lime-based waste material such as blood cockle shells (BCS) is a low-cost alternative to GML for remediating metal-contaminated soil.

Calcium carbonate ($CaCO_3$) is the major component of BCS [7]. Alkalinity of BCS can be further increased by calcination, whereby $CaCO_3$ is converted to CaO during thermal degradation at high temperature. The presence of CaO increases the pH of soil and is essential for effective immobilization of Pb.

Biochar is a carbon-rich material and is produced by pyrolysis process, whereby waste biomass is heated in an oxygen-limited condition [8]. Biochar is usually used to improve soil functions and biodiversity by retaining moisture and nutrients in the soil [9]. Pyrolysis of palm kernel shells (PKS) and BCS produces a new composite biochar (CPB) that possesses high pH value. Furthermore, residual ash from the combustion of PKS and BCS may react to produce liming material that is milder in alkalinity and lasts longer in soil [10].

Increasing peak pyrolysis temperature and heating duration may increase the pH of biochar [11].

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To the best of our knowledge, the effect of BCS content in composites on the pH of CPB has not been reported elsewhere. Therefore, the main objective of this work was to produce CPB suitable for immobilization of soil Pb. In order to produce CPB with high pH value, a series of operating parameters such as weight ratio of PKS-to-BCS, pyrolysis temperature and pyrolysis duration are analyzed and discussed in this research paper.

MATERIALS AND METHODS

Materials

Palm kernel shells (PKS) and BCS were obtained from an oil palm mill in Jengka, Pahang and Sabak Bernam beach, Selangor, respectively. Ethanol, buffer solution, sodium acetate solution (NaOAc), and ammonium acetate solution were purchased from Aras Bakti Sdn Bhd. Standard lead (Pb) was purchased from Sigma-Aldrich.

Preparation of CPB

The PKS sample was sun-dried for 48 hours and oven-dried for 48 hours. The BCS sample was boiled with deionized water for 2 hours, and air-dried for 72 hours. Then, PKS and BCS were ground and sieved to 2 mm and 75 μm, respectively. Composite biochar (CPB) was prepared by pyrolyzing homogenized PKS and BCS at various weight ratios (i.e., 1:0, 10:1, 5:1, 1:1, and 0:1), peak pyrolysis temperatures (i.e., 500°C, 700°C, and 900°C), and heating durations (i.e., 1, 2, and 3 hours) with a tube furnace under nitrogen atmosphere.

Physico-chemical Characterization of CPB

The pH value of CPB was measured on a slurry with samples-to-water ratio of 1:10 (w/v) using a calibrated pH meter. Proximate analysis on CPB was determined using a TGA (TGA/DTG, Netzsch, Tarsus) under N_2 gas condition at heating rate of 10°C/min to peak temperature of 900°C [12]. Elemental composition for CPB was determined by XRF (Spectro X-lab 200), while crystalline phases were estimated by XRD.

Soil Sampling

Soil was collected from the berm of a shooting range located at Sungai Besi Army Camp, Kuala Lumpur. An auger sampler was used to collect soil samples at a depth of 20 cm from surface. The collected soil was air dried and passed through a 2 mm sieve.

Soil Amendment and Incubation Study

Soil samples were homogenized with CPB9 in plastic zip lock bags at various application rates (i.e., 1, 3, and 5 % (w/w)) and incubated at 25°C for 21 days to ensure sorption occurred between Pb and the soil. This method was adapted from Ahmad et al. [13] and Salleh, Ishak, & Yong [14]. Soil pH was recorded on a 1:10 ratio soil slurry using a calibrated pH meter every 3 days.

Selective Sequential Extraction (SSE)

After soil incubation by using CPB9 with 5% (w/w) application, analyses of selective sequential extraction (SSE) were carried out according to Table 1 [15]. The concentration of Pb in the exhangeable, carbonate, Fe-Mn oxide, organic, and residual fractions was analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

RESULTS AND DISCUSSION

pH of CPB

Table 2 shows the pH values of CPB produced at various PKS-to-BCS weight ratios, peak pyrolysis temperatures, and heating durations. Composites that were pyrolyzed at 700ºC, for 2 hour with weight ratio of (1:1) produced the highest pH (12.6) compared to those with ratios 10:1 and 5:1, as shown in Figure 1. Increasing the content of BCS increased the pH value of CPB. This is due to the fact that BCS contains about 95% w/w of alkaline material (i.e., $CaCO_3$) in the composite [7]. Furthermore, the pH value for CPB increased with increasing peak pyrolysis temperature (Figure 1). The $CaCO_3$ content in BCS may be converted to CaO at high temperature [16]. CaO is an

Table 1. Selective sequential extraction procedure [15]

Fraction	Extraction reagents	Extraction conditions
Exchangeable	8.0 mL of 1.0 mol dm^{-3} MgCl$_2$	Continuous agitation, 25°C, 1h
Carbonate	8.0 mL of 1.0 mol dm^{-3} NaOAc	Continuous agitation, 25°C, 5h
Fe-Mn oxide	20 mL of 0.04 mol dm^{-3} NH$_2$OH.HCl	Occasional agitation, 96°C, 6h
Organic	First, 3.0 mL of 0.02 mol dm^{-3} HNO$_3$	Occasional agitation, 85ºC, 2h
	Next, 5.0 mL of 30% (v/v) H$_2$O$_2$ and 3.0 mL of 30% (v/v) H$_2$O$_2$	Next, occasional agitation, 85ºC, 2h
	Last, 5.0mL of 3.2 mol dm^{-3} NH$_4$OAC in 20% (v/v) HNO$_3$	Last, agitated continuously, 0.5h
Residual	5 mL, HCl, HNO$_3$	Acid digestion by ICP-OES

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alkaline earth metal oxide with a very weak Lewis acidity of metal cation due to its small electronegativity. Hence, conjugate anion (oxygen) displays strong basic properties [17].

Increasing peak pyrolysis temperature enhanced the alkalinity of CPB. As shown in Figure 2, CPB8 had the highest pH value (12.7) when pyrolyzed at the highest peak pyrolysis temperature (900°C). Biochar produced at high temperature contains inorganic carbonates that are alkaline in nature. This increase of pH of CPB was probably due to the decomposition of acidic functional groups and volatilization of organic acids from CPB [18].

The pH value of pyrolyzed composites with PKS-to-BCS weight ratio of 1:1 increased as heating duration increased from 1 to 3 hours. Based on Figure 3, the highest pH value was recorded on CPB8 and CPB10 (12.7) that were pyrolyzed at 900ºC for 2 hours. At this stage, the pyrolysis process caused degradation of volatile matter of the composites. As such, there was insignificant difference in pH of CPB produced at 1-3 hours of heating duration. Therefore, CPB produced at weight ratio of 1:1 and peak pyrolysis temperature of 900°C for 1 hour was chosen for soil Pb immobilization study.

Table 2. Conditions for pyrolysis and pH values of CPB

Sample	PKS-to-BCS weight ratio	Heating duration (hours)	Peak pyrolysis temperature (°C)	pH
CPB1	1:0	2	700	10.3
CPB2	10:1	2	700	8.9
CPB3	5:1	2	700	11.1
CPB4	1:1	2	700	12.6
CPB5	0:1	2	700	12.3
CPB6	1:1	2	500	10.2
CPB7	1:1	2	700	11.1
CPB8	1:1	2	900	12.7
CPB9	1:1	1	900	12.5
CPB10	1:1	2	900	12.7
CPB11	1:1	3	900	12.3
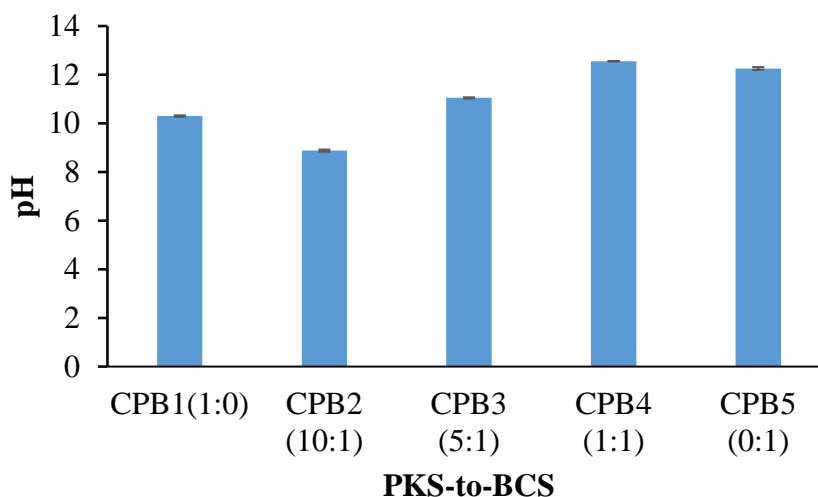
Figure 1. pH of CPB as a function of PKS-to-BCS weight ratio

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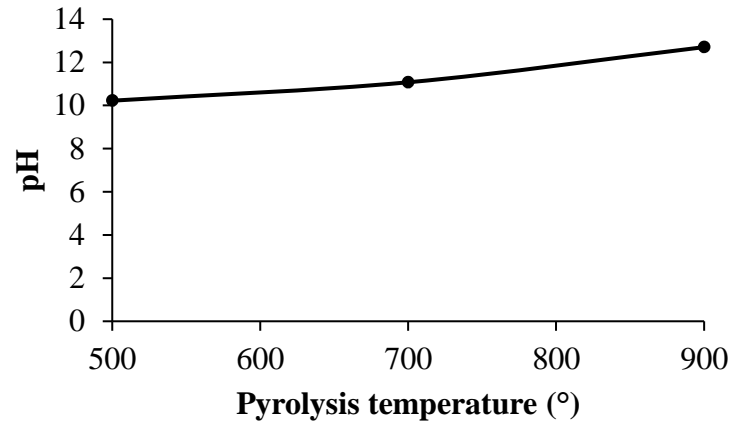bilizing Lead in Shooting Range Soil

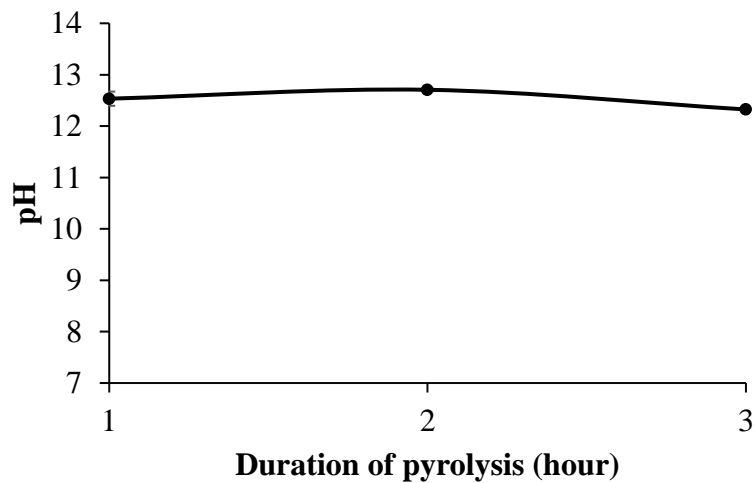**Figure 2**. pH of CBP as a function of peak pyrolysis temperature (°C)

Figure 3. pH of CPB as a function of heating duration (hours)

Proximate and Ultimate Analysis Optimized CPB

Table 3 shows proximate and ultimate analyses for raw composites of PKS and BCS (1:1 weight ratio). The composites had low moisture content (2.2% w/w) and high FC (43.3% w/w) and ash (35.0%) content.

Table 3. Proximate and ultimate analyses of PKS-to-BCS (1:1)

	Composition	Weight percentage (%w/w)
Proximate analysis	Moisture	2.2
	Fixed carbon	43.3
	Volatile matter	19.5
	Ash	35.0
Ultimate analysis	C	28.7
	H	2.9
	N	0.3
	S	0.3

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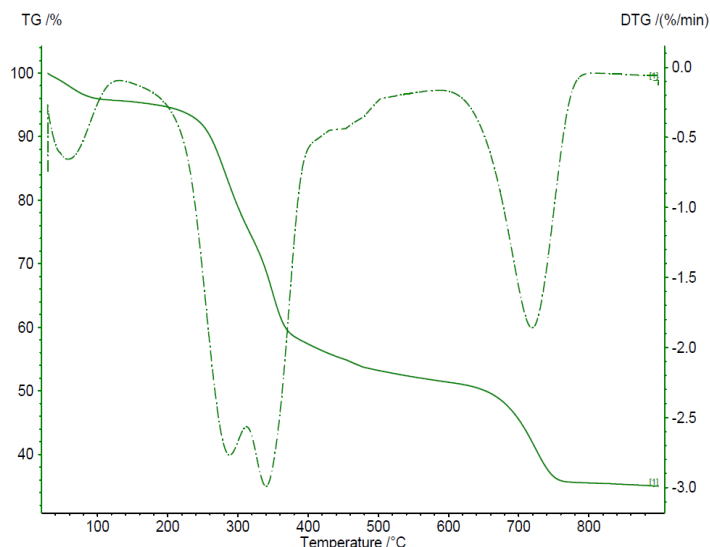bilizing Lead in Shooting Range Soil

Figure 4. TG/DTG thermogram of PKS-to-BCS (1:1)

TGA Analysis

The pyrolysis process on PKS and BCS composites at 1:1 weight ratio consisted of four stages of decomposition. The first stage of decomposition occurred at 100°C-150°C due to moisture removal [19]. The second stage occurred at 230°C-300°C from decomposition of hemicellulose. The third stage occurred at 340°C-380°C from degradation of cellulose . The fourth stage of decomposition at 390°C-760°C was due to slow degradation of lignin [20]. In addition, breakdown of $CaCO_3$ to CaO also occurred at this stage [17]. Similar results of hemicellulose, cellulose, and lignin degradation were also confirmed by Ma *et al.* [21] and Salleh, Pengiran Ismail & Yong [10].

XRF Analysis

Table 4 shows elemental composition (% w/w) for PKS, BCS, and CPB9. The major element in BCS was calcium (Ca) at 65.74% w/w. This finding agreed with that reported in literatures [22]. Iron (Fe), Ca, and silicon (Si) were also available in PKS. CPB9 contained a large amount of Ca that contributed to high pH.

XRD Analysis

Figure 5 shows XRD spectra for CPB9. In comparison with the standard Joint Committee of Powder Diffraction Society (JCPDS) file number 04-0777, CPB9 that was pyrolyzed at 900°C, $CaCO_3$ was completely converted to CaO. This evidence showed that the high pH values for CPB6-9 was due to the presence of CaO. The peaks of CaO are indicated by the circles. In a study conducted by Rezaie *et al.* [16], the XRD pattern for shells calcined below 700°C showed $CaCO_3$ as the main component, and when calcined at higher temperature the peak of CaO emerged.

Table 4. Elemental composition of PKS, BCS, and CPB9

PKS:BCS sample	Elemental composition (%)				
	Ca	Si	Fe	Al	Ag
PKS	1.15	0.81	4.25	0.04	0.30
BCS	65.74	0.02	0.09	0.01	0.22
CPB9	43.17	0.34	3.97	0.07	0.13

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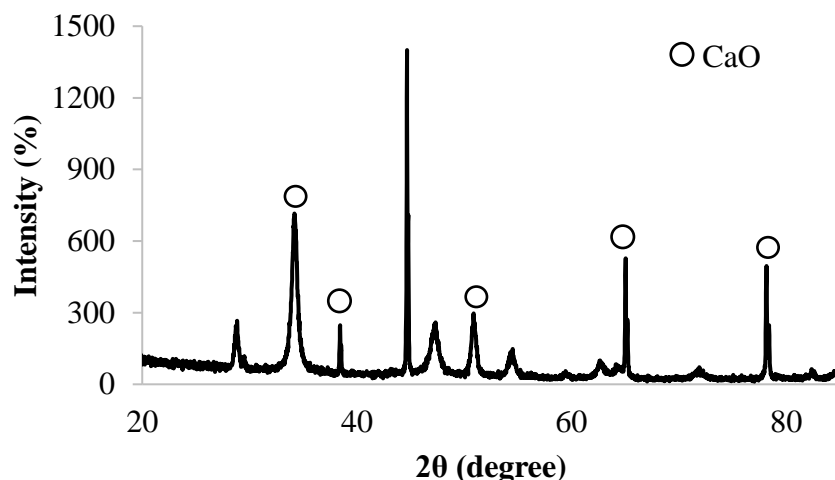bilizing Lead in Shooting Range Soil

Figure 5. XRD spectra of CPB9

Amendment of CPB on Soil pH

Figure 6 shows average pH of soils amended with CPB9 at 1%, 3%, and 5% w/w for 21 days. In this work, the soil incubation was carried out at 25°C for 21 days. Based on our findings, 21 days or 3 weeks should be enough to get the preliminary trends of the immobilization test. This duration is enough for sorption between heavy metal ions and soil. Emendation of soil samples with CPB9 at 1-5% w/w showed increased soil pH due to the chemical reaction of the alkaline CaO with soil moisture. Increasing application rate of CPB9 increased soil pH. The high content of Ca (i.e., 65.7%) in CPB9 played a significant role in increasing soil pH and reducing soil acidity. Amendment with 5% w/w of CPB7 increased

soil pH value from 6.4 to 12.0. The major chemical constituent of CPB9 was CaO, which contained Ca^{2+} cations that may neutralize soil solution by displacing H^+ [14]. The reaction of Ca^{2+} with H^+ can form Ca^{2+} and H_2O and thereby resulting in increased soil pH [23]. By increasing the application rate of CPB9, acid neutralizing capacity (ANC) increased and increased the soil pH during incubation. Besides, ash produced from pyrolyzed PKS formed pozolanic materials such as calcium aluminosilicate hydrates (CAH) and calcium silicate hydrates (CSH) when ash reacted with CaO from pyrolyzed BCS [24]. This formation may form cement in the treated soil which has high strength and low swell and responsible for heavy metal immobilization through inclusion, surface sorption, and physcial entrapment [25].
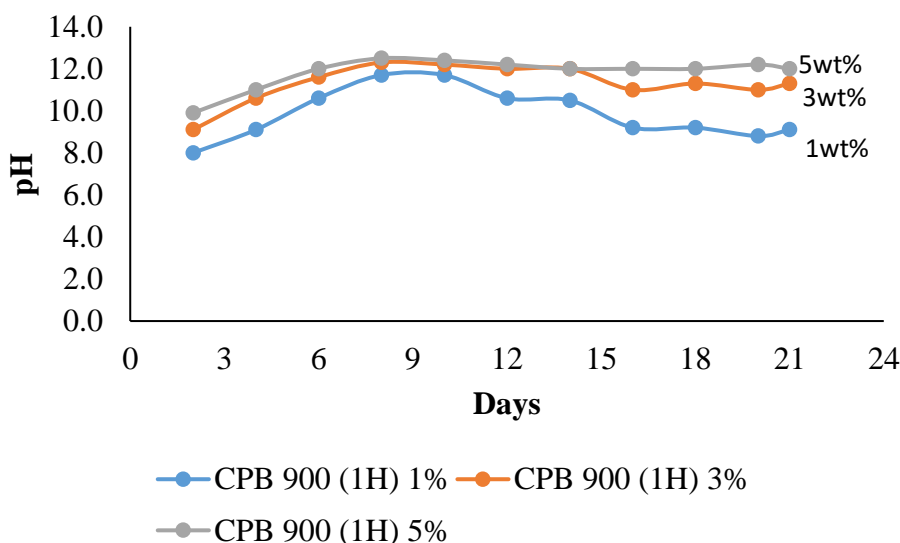

Figure 6. Average pH of soils amended with CPB9 at 1%, 3%, and 5% w/w for 21 days

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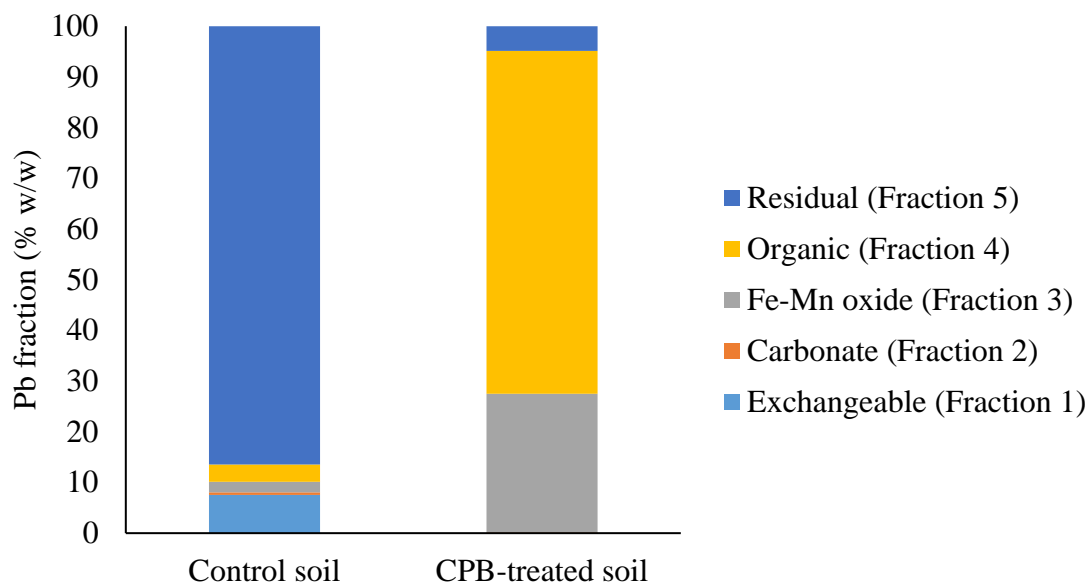bilizing Lead in Shooting Range Soil

Figure 7. Distribution of Pb (% w/w) in the selective sequential extraction (SSE) fractions (exchangeable, carbonate, Fe-Mn oxide, organic, residual) of control and CPB-treated soils at 5% (w/w)

Table 5. Exchangeable of Pb and pH in the soil as treated with eggshells and biochar

Material for treatment	Soil pH		Exchangeable Pb (%)		References
	Control	After treatment	Control	After treatment	
Egg shells	6.74	8.13	0.70	0	[5]
5% w/w spent mushroom substrate biochar	4.69	7.73	0.60	0	[4]
5% w/w CPB9	6.40	12.00	7.56	0.01	This study

Selective Sequential Extraction (SSE)

Figure 7 shows distribution of Pb fractions (% w/w) in the selective sequential extraction of the control and CPB-treated shooting range soils. The CPB-treated soil had the highest percentage of Pb in the organic fraction (67.6%), followed by Fe-Mn oxide (27.35%), residual (4.86%), carbonate (0.15%), and exchangeable (0.01%). This result indicated that Pb was mostly associated with the organic matter (i.e., biochar) in the CPB-treated soil. Furthermore, the percentage of Pb in exchangeable and carbonate fractions decreased from 7.56% to 0.01% and 0.51% to 0.15%, respectively. This indicated that applying CPB reduced the availability of Pb in soil, possibly by coordination/complexation of soluble Pb^{2+} ions with the organic substance [26]. The increase pH of the CPB-treated soil may cause precipitation of soluble Pb and limits the strength of reagent (NaOAc) to dissolve Pb in the carbonate fraction [5]. At pH>5, Pb hydroxide precipitate was coverted to a less soluble

PbO through oxidation process [2] . At high pH value, there are more negative charges on the surface due to deprotonation of the biochar [8], consequently increases the CEC value and more Pb^{2+} ions are bound to the biochar.

The exchangeable Pb of CPB was compared with those from the low-cost calcium carbonate-based materials such as eggshells and spent mushroom substrate biochar (SMSB) (Table 5). The soil pH value increased from 6.74 to 8.13 and the exchangeable Pb decreased from 0.7% to 0% when the soil was treated with egg shells. Similarly, the soil pH increased from 4.69 to 7.73 and the exchangeable Pb decreased 0.6% to 0% when the Pb contaminated soil was treated with spent mushroom substrate biochar. For CPB, the soil pH increased from 6.4 to 12 at an application rate of 5% (w/w). Despite the high exchangeable Pb in control soil, application of CPB decreased the exchangeable Pb to near zero and was comparable with egg shells and spent mushroom subtrate biochar.

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The major constituent of CPB was CaO while egg shells and SMSB mostly consisted of $CaCO_3$. As a result, CPB had higher alkalinity compared to other materials and had higher potential to precipitate Pb in soil. The increase of the soil pH would decrease the solubility of Pb and effectively reduced the mobility of metal, as shown in Figure 7. CPB could be implimented to shooting range soil by mouldboard ploughing or rotatory spading to the subsurface of contaminated soil. CPB should be in fine particle form in order to have a good distribution during the application process to increase the concentration of total alkalinity as CPB has high pH. CPB seemed to be the most suitable alkaline subtance for treating Pb by increasing and maintaining the high pH of the soil.

CONCLUSION

CPB with the highest pH value (12.7) was produced by pyrolyzing PKS and BCS at a weight ratio of 1:1 at peak pyrolysis temperature of 900°C for 1 hour. The pyrolysis process changed the composition of the powdered BCS waste from $CaCO_3$ to CaO, which was more alkaline as the main significance that affected the mobilization of Pb in soil. The shooting range soil treated with CPB9 5% w/w had the soil pH increased from 6.4 to 12.0, which was alkali. The composition of ash from pyrolyzed PKS waste caused the high soil pH maintained throughout the period of soil incubation which was 21 days. Furthermore, the result from SSE indicated a reduction of metal availability. The concentration of Pb in the exchangeable fraction (Fraction 1) decreased from 7.56% to 0.01% and carbonate fraction (Fraction 2) from 0.51% to 0.15% after the soil was treated with CPB9. Finally, the result in this study indicated that PKS and BCS waste could be used as an effective soil remediation for soil contaminated with heavy metal Pb.

ACKNOWLEDGEMENTS

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