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IMMOBILIZATION OF LEAD IN SHOOTING RANGE SOIL USING BIOCHAR FROM SPENT MUSHROOMSUBSTRATE

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ABSTRACT

Spent mushroom substrate (SMS) was pyrolyzed at 450°C for 2 hours and characterized using elemental analyzer and Boehm titration. Shooting range soil was incubated with 2.5% w/w and 5.0% w/w of SMSB for four weeks and the soil were characterized on the elemental composition, pH, electric conductivity (EC) and cation exchange capacity (CEC). The mobility of Pb in the incubated soil were studied using a modified selective sequential extraction (SSE) scheme. Total Pb in shooting range soil is 29385.5 mg/kg. The texture of shooting range soil is loamy sand with an average soil pH of 4.69, EC value 0.17 mS/mand CEC value 6.0 mEq/100g. After treatment with SMSB, the soil pH and CEC were increased and the concentration of exchangeable Pb decreased. Conclusively, this study found that there is potential in using SMSB for remediating Pb contamination in the shooting range soil.

Keywords: Spent mushroom compost; charcoal; black carbon; immobilization.

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1. INTRODUCTION

Shooting range contains high content of lead (Pb) due to long term deposition of lead shots. Total Pb concentration in Malaysian shooting range soils may be as high as 17,278 mg/kg [1]. Metallic Pb may be corroded to form hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), cerussite ($PbCO_3$), and massicot (PbO) within a week of atmospheric exposure [2]. Lead is toxic especially for children, as it attacks the developing brain and central nervous system. High level exposure of Pb through inhalation or ingestion may cause coma, convulsions and even death to human. Effective removal of soil Pb may be achieve by the costly soil washing technique. Alternatively, leaching of Pb from shooting range soil may be achieved by immobilization technique, using cheap liming minerals such as ground magnesium limestone, basalt or spent mushroom substrate (SMS).

Spent mushroom substrate is a waste biomass from the mushroom cultivation industry. About 5 kg of SMS is produced per kg production of mushroom and most SMS is reprocessed as agricultural compost or disposed by incineration and landfilling [3]. In fact, SMS have been studied for decontamination of acid mine drainage [4]. The abundance and high alkalinity of SMS makes it an ideal material for immobilization of Pb in shooting range soil. Spent mushroom compost contain carbon-rich sawdust, and is recommended as feedstock for biochar production [5]. In fact, SMS has been converted to biochar for removal of ammonia-N from the aqueous system [6]. Spent mushroom compost may be pyrolyzed at a low oxygen environment to produce a relatively stable, carbon-rich material called biochar, minimizing microbial degradation that releases pollutants from SMS into the environment. To the best of our knowledge, the potential of SMSB for immobilization of soil Pb has not been investigated. This study aims to (i) synthesize and characterize SMSB; (ii) elucidate the immobilization of Pb in shooting range soil by SMSB.

2. RESULTS AND DISCUSSION

2.1. Physico-chemical Properties for SMS and SMSB

The yield of SMSB from pyrolysis of SMS was 35% w/w. Similar to other biochar, SMSB has a higher pH (i.e., 9.73) compare to SMS feedstock (i.e., 7.5), possible due to the presence of alkaline minerals in the burnt ash. The CEC value for SMSB (i.e., 9.5 mEq/100g) is slightly higher than those of shooting range soil (i.e., 6.0 mEq/100g). Ash content for SMS and SMSB are similar (i.e., 27.7% w/w and 27.8% w/w respectively) and is slightly higher than that of rubber wood sawdust (22.7% w/w) [7], due to the addition of lime ($CaCO_3$) during the preparation of SMS [8].

The elemental composition (% w/w) for SMS, SMSB and HCl-SMSB are shown in Table 1. Pyrolysis process on has increased percentage of C and H contents, and decreased that of O and N for SMSB. The H/C molar ratio for the SMSB (i.e., 0.3) was lower than that of SMS (1.6), indicating that SMSB is more stable than SMS [9]. Treatment of 1.0 M HCl has removed 21.3% w/w of soluble fraction from the ash from SMSB, most of which are Ca (10% w/w) and K (0.4% w/w). However, heavy metals such as Cr, Pb and Zn remains unchanged. This indicates that the toxic heavy metals in SMSB are stable and are not soluble in water. The acidic functional groups on the surface of the HCl-treated SMSB consists of primarily carboxylic (0.3 mmol/g) and phenolic groups (0.5 mmol/g). The amount for basic functional groups for SMSB was 0.2 mmol/g.

Table 1. Elemental composition (% w/w) for SMS, SMSB, and HCl-treated SMSB

Elements	SMS	SMSB	HCl-Treated SMSB
C	44.0	53.3	72.8
O	21.4	11.1	18.6
H	5.8	2.6	2.0
N	1.0	0	0.1
S	0.1	0	0
Ca		12.8	2.8
Cr		0.1	0.1
K		0.5	0.1
Mg		0.8	0.8
Pb		0.2	0.2
Zn		0.1	0.1

2.2. Physico-chemical Properties for Shooting Range Soil

Table 2 shows the physico-chemical properties of shooting range soil. The soil type is of loamy sand, which consists of 73%, 15% and 12% of sand, silt and clay respectively. The soil pH is 4.69 and is classified as very strongly acidic [10]. Shooting range soil has a very low organic content, as indicated by the low SOM (3.8% w/w) and SOC contents (2.2% w/w). The total metal contents of shooting range soil is shown in Table 3. Total soil Pb content is 29385.5 mg/kg, and is significantly higher than the Malaysian recommended site screening levels for soil Pb (i.e., 800 mg/kg) [11]. Low soil CEC value (6.0 mEq/100g) conforms to those of a loamy sand soil. The combination of high soil Pb, low soil pH and CEC may lead to leaching of Pb ions into water resources.

Table 2. Physico-chemical properties for shooting range soil

Soil Parameters	Average Value
pH	4.69 ± 0.15
EC (mS/m)	0.17
Moisture (% w/w)	13 ± 2.49
CEC (mEq/100g)	6.0
% Sand	73
% Silt	15
% Clay	12
SOM (% w/w)	3.8 ± 0.94
SOC (% w/w)	2.2 ± 0.55

Table 3. Total metal (mg/kg) of shooting range soil

Metal	Total Content (mg/kg)
Pb	29385.5 ± 3308.1
Fe	11906.7 ± 167.4
Cu	7109.4 ± 8623.5
K	3778.5 ± 1006.8
Zn	1054.8 ± 1120
Mg	536.4 ± 66.6
Ca	305.7 ± 1.3
Mn	189.9 ± 2.6
Na	134.3± 31.7

2.3.Soil Incubation and Characterization

The images of the texture of shooting range soils after incubation with 5 % w/w SMS and 5 % w/w SMSB are shown in Fig.1. The presence of SMS and SMSB has cause aggregation of fine soil particles, forming course granular, and friable soil aggregates. This is due to the increasing soil organic matter, due to the addition of SMS and SMSB. The presence of SMSB has given a darker appearance to the soil colourFig.1. (iii).

(i) (ii) (iii)

Fig.1. Shooting range soils (i), incubated with (ii) 5 % w/w SMS; and (iii) 5% w/w SMSB

The pH and CEC values for incubated soil are shown in Table 4. The increasing application of SMSB has proportionally increased the pH value of shooting range soil. Incubation with 2.5% w/w and 5.0% w/w SMSB has increased the pH of shooting range soil from 4.69 to 5.56 and 7.73 respectively. The alkaline minerals in the ash of the SMSB has neutralized the acidity in shooting range soil. The CEC values for the incubated soil samples were also increased slightly from 6.0 to 6.7 and 7.0. The introduction of porous and negative-charged surface of SMSB may have increased the CEC values of shooting range soil [12]. Furthermore, the increased soil pH after incubation with SMSB may also induced deprotonation of functional groups on the surface of soil particles and organic matter, and contributed to higher CEC values for the SMSB-incubated soil, and providing more available binding sites for retention of Pb ions.

Table 4. Physico-chemical properties of SMSB-incubated shooting range soil at 0.0, 2.5, 5.0 % w/w of application rate

Property	**Application Rate (% w/w)**		
	0.0	**2.5**	**5.0**
pH	4.69	5.56	7.73
CEC, mEq/100g	6.0	6.7	7.0

2.4.Modified Selective Sequential Extraction

Table 5 shows the distribution of Pb (% w/w) in the five fractions of the SSE experiment. The exchangeable Pb for shooting range soil (CTR) was 0.6%. Incubation with 5% w/w SMS and 5% w/w SMSB have reduced the exchangeable Pb to 0.4% w/w and 0.0% w/w respectively. Shooting range soils that were incubated with SMS and SMSB have significantly higher carbonate-bound Pb fraction, increased from 4.9% w/w (CTR) to 71.5% w/w and 77.1% w/w respectively. Conversely, incubation with SMS and SMSB decreased the organic bound Pb for CTR (77.4% w/w) to 9.6% w/w and 6.4% w/w respectively. These changes may indicate: (1) precipitation of available Pb ions to Pb carbonate from the increase of soil pH; (2) mobilization of organic bound Pb (i.e., Pbhumate) and transformation to carbonate bound Pb due to high soil pH. Most of the Pb in shooting range soil was bound to the existing organic matter in the soil. When both SMS and SMSB were incubated, shooting range soils were introduced with the alkaline Ca minerals (i.e., calcium carbonate and calcium oxide). The increase of soil pH may have hydrolyzed existing soil carbon to soluble fraction, but the presence of hydroxide ions in the alkaline soil may have formed Pb hydroxide, and eventually to Pb carbonate [13].

Table 5. Distribution of Pb (% w/w) in the selective sequential extraction (SSE) fractions (exchangeable, carbonate, Fe/Mn oxide, organic and residual) for shooting range soil (CTR) and incubated soils (5% SMS and 5% SMSB)

SSE Fractions	Pb (% w/w)		
	5% SMS	5% SMSB	CTR
Exchangeable	0.4	0.0	0.6
Carbonate-bound	71.5	77.1	4.9
Fe/Mn oxide-bound	15.7	13.3	12.4
Organic-bound	9.6	6.4	77.4
Residual	2.7	3.1	4.7

3. EXPERIMENTAL

3.1. Sampling and Preparation of SMSB

Spent mushroom substrate (SMS) were collected from an oyster mushroom (i.e., Pleurotusostreatus) farm at Gerisek, Johor (GPS coordinate: 2.233387, 102.700237). The as-received SMS was autoclaved, oven-dried at 60°C for 5 days and sieved using a 2-mm mesh screen. Spent mushroom substrate biochar (SMSB) was prepared by pyrolyzing SMS in a furnace at 450°C for 2 h under nitrogen atmosphere Fig. 1. Hot SMSB was quenched and rinsed thoroughly with deionized (DI) water, oven-dried at 100°C for 24 hours and sieved to particle size of 150 µm. The yield of SMSB (% w/w) was calculated with Equation (1):

$$\%Yield = \frac{W_c}{W_{ds}} \times 100 \quad (1)$$

whereWc and Wds are the weights for SMSB (g) and dried SMS (g) respectively.

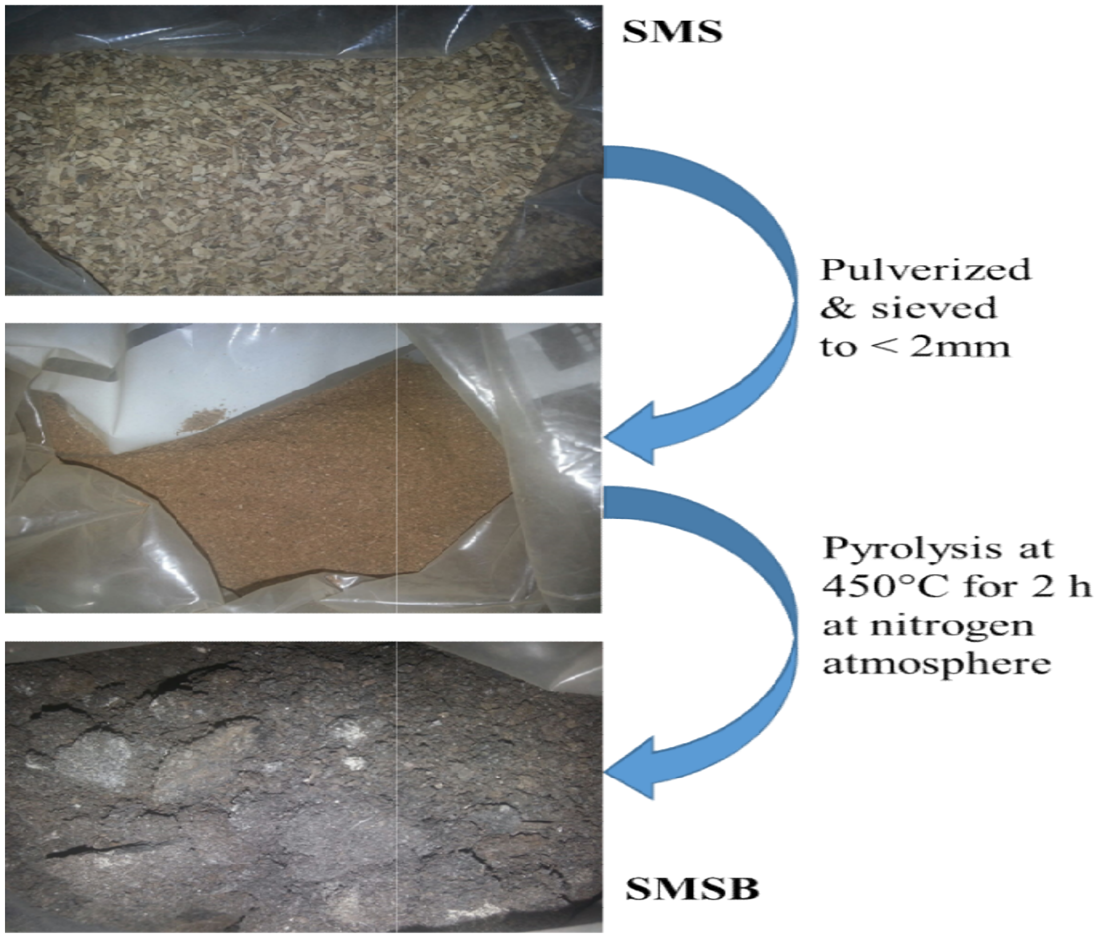

Fig.1. Preparation of SMSB from SMS

3.2.Sampling and Preparation of Shooting Range Soil

Soil samples were collected at Royal Malaysian Police Forces Shooting Range at Kuala KubuBharu, Selangor, Malaysia (GPS coordinates: 3.575858, 101.667350). The soil samples were collected at ten sampling points using an Auger sampler at a depth of 30 cm from the soil surface. The soil sample was air-dried for 3 days and sieved with a 2-mm mesh screen. Lead shots were removed manually and the air-dried soil samples were stored in plastic zip-lock bag.

3.3.Physico-Chemical Characterization for SMS, SMSB and Shooting Range Soil

The pH and EC values for shooting range soil and SMSB were determined using a calibrated pH/EC meter. pH values were measured on DI water slurry at 1:1 solid-solution ratio, while EC values were measured from the filtrates of DI water slurry at 1:5 solid-solution ratio. Soil particle distribution was determined with the hydrometer method [14]. The cation exchange capacity (CEC) for shooting range soil and SMSB was determined using USEPA Method

9081 [15]. Soil organic matter (SOM) was determined using the loss-on-ignition (LOI) method [16], and the soil organic carbon (SOC) was calculated using Equation (2)[17]. Inorganic carbon (IC) content for shooting range soil were determined from a DI water extract (soil/solution ratio: 1:2) and analyzed with a TOC analyzer (Shimadzu TOC-V/TN). Inorganic ash component in SMSB was eliminated by agitation with 0.05 M HCl, DI water, and 0.05 M $CaCl_2$ solution. The HCl-treated SMSB was oven-dried at 100°C for 12 h and the surface functional groups for SMSB was determined using Boehm titration method [18]. Air-dried soil samples and SMSB were digested using aqua-regia[19], filtered and analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Perkin Elmer DV7300), and the total metal content (mg/kg) in soil samples were calculated according to Equation (3).

$$SOC = \frac{SOM}{1.72} \quad (2)$$

$$\text{Total metal content} = [\text{metal}] \times V / m_{soil} \quad (3)$$

where [metal] is the concentration of metal ion in digested solution, V is the volume of digested solution and m_{soil} is the mass of soil sample (kg).

3.4.Soil Incubation and Characterization

Shooting range soil was mixed with SMSB at two application rates of 2.5% and 5.0% w/w. The shooting soils were again incubated with SMS and SMSB at 5% w/w application rate and were further analyzed using the modified SSE scheme. All soil samples were incubated for four weeks at room temperature (25°C). Soil moisture contents were maintained at field capacity by frequent watering using DI water. The pH and CEC values of the incubated soils were determined as described earlier.

3.5. Modified Selective Sequential Extraction

A modified SSE scheme that consist of 5 fractions (i.e., exchangeable, carbonate-bound, Fe/Mn oxides-bound, organic-bound and residual) (Table 6) was adopted [20]. One gram of the incubated soil sample was extracted in a 50 mL centrifuge tube and the soil-solution mixture was agitated using an end-over-end shaker. Then, the mixture was centrifuged at 15,000 rpm for 10 min, decanted and the residue soil was washed twice with 5 mL of DI water. The supernatants were collected from each steps of extraction and was diluted to 50 mL using DI water. The Pb concentration of the extracts was analyzed with ICP-OES. The percentage of Pb in each fractions (Pb_f) were calculated using Equation (4).

$$Pb_f(\%w/w) = \frac{[Pb]_f \times V_f}{m_{Soil\_Pb}} \times 100 \qquad (4)$$

where $[Pb]_f$ is the concentration of Pb (mg/L), V_f is the volume of fraction (L) and m_{soil_Pb} is the total mass of Pb is the shooting range soil (mg).

Table 6. Reagents and conditions for the modified Selective Sequential Extraction (SSE)

Step	Fraction	Reagent	Agitation Time/Temperature
1	Exchangeable	8 mL of 1.0 M $MgCl_2.6H_2O$ (pH 7)	1 h at 25°C
2	Carbonate-bound	8 mL of 1.0 M CH_3COONa (pH 5)	3 h at 25°C
3	Fe/Mn oxides-bound	20 mL of 0.04M $NH_2OH.HCl$ in 25% (v/v) CH_3COOH	Occasional agitation for 6 h at 95°C
4	Organic-bound	5.0 mL of 30% v/v H_2O_2 (pH 2), 3.0 mL of 0.02 M HNO_3;	2 h at 85°C
		3.0 mL of 30% v/v H_2O_2 (pH 2); cool, add 5.0 mL of 3.2 M	2 h at 85°C
		CH_3COONH_4 in 20% v/v HNO_3	0.5 h at 25°C
5	Residual	9 mL 37% HCl& 3 mL HNO_3	Microwave digestion EPA Method 3051 [19]

4. CONCLUSION

Based on the result obtained in this study, the properties of soil were improved by application of SMS and SMSB. The increased of pH and CEC of the SMSB-incubated soil may help reduce leaching of Pb from soil. In the SSE experiment, the significant reduction of exchangeable Pb upon treatment with SMSB shows its potential as amendment for immobilization of Pb in shooting range soil. Based the incubation experiment setup, the presence carbon in the SMSB-incubated soil did not show immediate interactions with Pb. Further studies on the long-term SMSB incubation on soil Pb speciation is warranted to understand SMSB's overall Pb immobilization mechanism.

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