Characterization and performance of low cost amendments to immobilize lead in contaminated soil

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Abstract. Immobilization is a method of remediation to reduce lead (metals) mobility by soil amendments to prevent from uptaking of plant roots and ground water contamination. This research aims to produce, characterize, and assess the efficacy of low cost solid amendments in immobilizing lead in naturally contaminated soil. Biochars [produced from chicken manure (CM), chicken bone (CB), farmyard manure (FM)] and bioslurry (BS) were characterized with FTIR, SEM, and XRF. Amended soils were incubated and sequentially extracted prior to Pb measurement with AAS. Chars were made by pyrolysis at 450 °C for 90 minutes. Characterization data from FTIR showed that all amendments had similar spectra showing the existence of hydroxyl, carbonyl, C=C, C-H, C-O-C groups in the amendments. SEM images showed porous structure of the chars having pores diameter between 1.95 and 13.4 µm. XRF spectra revealed that dominant elements possessed by amendments were Ca, Na, Si (BS & FM), and P (TA & CM). The immobilization study showed that performance order from the most effective was CB > CM > FM > BS. Chicken bone biochar (CB) was the best amendment which immobilized up to 79.71% Pb and remediated soil from very high contamination-moderate risk into low contamination-low environmental risk status.

1. Introduction
Lead contaminated agricultural soil has become a global problem because of its risks to the health of living organism through food chain. Lead in soil can also contaminate groundwater. Human activities such as mining, smelting, agriculture and industry have played an important source of Pb in soil. Heavy metal is non-biodegradable and possesses long-term persistence in soils [1], therefore effective remediation measures are needed [2].

Remediation of Pb contaminated soil by conventional techniques such as excavation, soil washing and landfiling are costly and not suitable for agricultural soil in developing countries [2]. A sustainable method with low energy input, improving soil quality, and adding economic benefits is being sought [3]. Phytoextraction and immobilization are the two methods of in situ soil remediation which are considered the most appropriate because they are cheap, potentially maintain the structure and function of soil, and are most socially accepted. Phytoextraction and immobilization are contradictory in situ methods in remediation of lead-contaminated agricultural soil. Phytoextraction exploits plant ability in taking up Pb, so that efforts to increase Pb solubility in soil solution are needed. On contrary, immobilization focuses on reducing lead mobility by soil amendments to prevent from up taking of plant roots and ground water contamination.
Soil lead immobilization with low cost amendments is promising soil remediation for developing country. Biochar, carbonaceous porous material produced from pyrolysis of biomass, has widely applied due to its alkaline and good sorptive properties for metals and organics [4, 5]. Besides the wide application as soil ameliorant in agricultural cultivation [6], alkaline and nutrient rich slurry biogas has been used to remediate heavy metals from polluted soils and reduce Pb levels in soil extraction and test plant seeds [7]. Bioslurry also detoxifies Hg demonstrated by increased activity and weight of microbial biomass [8].

Environmental risk assessment of metal contamination in soil can be better performed by sequential extraction procedure (SEP) proposed by the Community Bureau of Reference (BCR) than conventional metal total concentration [9, 10]. In SEP, metal concentration in the most mobile fraction is distinguished from other more stable fractions. In BCR procedure, metal in soils is defined operationally into four geochemical fractions / phases i.e, acid extractable (F1), bound to Fe/Mn oxides (F2), bound to organic matter (F3, and residual fraction (F4). Acid extractable is the most mobile fraction and percentage of F1 determines the environmental risk of the metal [9, 11-13].

Surface properties, pH, and chemical composition of amendments are often associated with the ability of metal sorption and organic pollutants [14, 15]. Even so, there is still not enough information on the main properties that determine the effectiveness of Pb immobilization due to the level of contamination and soil properties [16]. Characterization of amendment material was carried out by FTIR, SEM, and XRF. The study was conducted by soil incubation techniques and continued by three-stage extraction using the modified Community Bureau of Reference (BCR) method and measurement of Pb concentrations by AAS. Objectives of this research are (i) to explore the properties of amendments, (ii) assess efficacy of low-cost amendments in influencing soil-Pb mobility, (iii) evaluate probable environmental risk of Pb in soil after immobilization.

2. Experimental

Amendment materials used in this research were collected from District Jaten and District Gondangrejo in Karanganyar Regency. Contaminated soil was collected from Cinangka, Bogor Regency. We prepared 4 low cost amendments from agricultural byproduct to minimize input of the immobilization process. Chars were made from chicken manure (CM), chicken bone (CB), farmyard manure (FM) by pyrolysis at 450 °C for 90 min in laboratory scale muffle furnace. Solid amendments were pulverized in a wooden mortar and filtered through 0.5 mm plastic filter and characterized with Fourier transform infrared (FTIR) spectroscopy to evaluate functional groups and XRF to perform elemental analysis. SEM was utilized to examine surface properties of the solid. Amended soils were incubated, measured of pH in water (1:2.5), and analyzed for loss of ignition (LOI) as a proxy to organic content. Incubation was conducted in 150 mL plastic container. Each 25 g of air-dried soil was admixed homogenously with 5% amendments, moistened, and incubated for 5 weeks in the dark at room temperature [17]. The incubated soil were checked and moistened weekly.

SEP with modified three steps BCR [9, 10] was carried out for studying redistribution of Pb into the geochemical phases after incubation of amendments. This method distinguishes metals into 4 fractions and is summarized in Table 1.

Table 1. Three step modified BCR sequential extraction procedure

| Fraction   | Procedure                                                                 |
|------------|---------------------------------------------------------------------------|
| F1 Acid extractable | Add 40 mL of 0.11 M acetic acid o 1.00 of soil sample. Shake for 16 h   |
| F2 Reducible    | Add 40 mL of 0.5 M NH₂OH.HCl (adjusted pH2 with HNO₃) to F1 residue. Shake for 16 h |
| F3 Oxidizable   | Add 10 mL of H₂O₂ 8.8 M, incubate at 85 °C for 1 h (Repeat procedure twice and cold). Add 50 mL CH₃COONH₄ (adjusted pH2 HNO₃). Shake for 16 h |
Residual Fraction (F4) remaining in the last step was extracted with aqua regia [1, 18, 19]. Solid solution separation between steps was done by centrifugation at 2500 rpm for 20 min. Solid was then washed with 20 mL deionized water, shaken for 15 min and centrifuged at 2500 rpm for 20 min. All metal quantification in each step was measured with atomic absorption spectrophotometer (AAS) Shimadzu AA 6500.

Impact to the environment was approached with the values of individual contamination factor (ICF) and Risk Assessment Code (RAC). ICF was the measure of retention time of the metal before reaching the environment and determined by dividing the sum of non-residual fractions by residual fraction (F4) [9, 13]; also called as ratio of secondary to primary phase, RSP [20]. RSP can be used to distinguish anthropogenic sources of heavy metal from natural sources. The value of CF expresses contamination degree. RAC (%F1) expresses risk or mobility of the metal/pollutant and is determined with the proportion of metal in F1 from the total metal concentration in soil. Immobilization efficiency (E) was employed to evaluate the effectiveness of the methods [21] and formulated as follow:

$$E = 100 \left( \frac{M_o - M_e}{M_o} \right)$$

$M_o$ : metal extract concentration in soil without amendment

$M_e$ : metal extract concentration in amended soil.

3. Results and discussions

3.1. Characteristics of soil and amendments

Table 2 shows the important physical-chemical properties of soil samples. Soil sample had acidic pH, loam texture, and rather low organic compound (LOI). Pb content is extremely high for agricultural soil in China, USA, and Australia [12]. Ceiling concentrations in China Soil quality standard for grade B and grade C are 350 and 500 mg/kg. Grade C includes upper limits to ensure agricultural production and plant growth and Pb content in contaminated soil exceeded 8 times of the standard. Also, it exceeded 10 times of U.S. EPA (400 mg/kg). Similarly, Australia has Health investigation level (HIL) A and C standard for residential with garden/accessible soil and open space respectively. Compared to Values of HIL A and HIL C for lead (300 and 600 mg/kg); the soil exceeded 13 times and 6 times of Australian standard.

Table 2. Physical-chemical properties of soil sample

| Texture (%) | Soil Texture (USDA) | Pb total ppm | EC mS/cm | pH | CEC me/100 g | LOI (%) |
|-------------|---------------------|--------------|----------|----|--------------|--------|
| Sand 2–0.05  | Silt 0.05-0.002     | Clay <0.002  | (USDA)   | ppm | EC mS/cm     | pH     | CEC me/100 g |
| 25.54       | 49.70               | 24.76 LOAM   | 4029     | 0.13| 5.5          | 17     | 8.45         |

FTIR spectra and SEM micrograph of the biochars were shown in Figure 1 and 2. FTIR data showed 9 peaks in FM spectra and 13, 14, 15 peaks in the spectra of CM, CB BS respectively. Some similar important peaks were tabulated in Table 3. Characterization data from FTIR showed that solid amendments had similar spectra indicating the existence of hydroxyl, carbonyl, carbonate, phosphate C=O, C-H, and C-O groups in the amendments [22]. Peak of hydroxyl group appeared at frequency of 3500 cm$^{-1}$ corresponded to OH bond stretching. Aromatic C=C and C=O peaks observed 1613 cm$^{-1}$ [15]. The peaks observed at 1420-1450 and 1034 cm$^{-1}$ showed that biochar also had abundant CO$_2^-$ and PO$_4^{3-}$. These functional groups can act as precipitation agent and sorption sites for Pb in soil. Carbonates and phosphates compound of Pb have low solubility. For example, hydroxyypromorphosite, Pb$_{10}$(PO)$_6$(OH)$_2$ K$_{sp}$ = ~ 10$^{-78}$ will be effectively reduce lead concentration in soil solution down to order of µg/kg.
**Figure 1.** FTIR spectra of chicken manure biochar (CM)

**Figure 2.** SEM photomicrograph of chicken bone biochar (CB)
Table 3. Peaks, area, and functional groups in the FTIR spectra of amendment

| Peak (cm⁻¹) | CB          | CM          | FM          | BS          | Note                     |
|------------|-------------|-------------|-------------|-------------|--------------------------|
| 1000-1050  | 1034.85(31.18) | 1040.64(23.17) | -           | 1036.78(23.30) | Phosphate; PO₄³⁻       |
| 1410-1465  | 1415.81(0.393); | 1417.74(-1.04); | 1448.6(0.008) | 1421.6(0.049) | C=O alcohol             |
| 1600-1700  | 1613.52(5.865) | -           | 1613.52(0.184) | 1643.42(0.039) | Carbonate; CO₃²⁻        |
| 2850-3000  | 2853.81(0.144); | 2855.73(0.004) | 2855.73(0.004) | 2852.84(0.02) | C=O carboxyl or ketones |
| 3420-3550  | 3421.87(20.09) | 3435.37(0.196) | 3439.23(0.031) | 3428.62(0) | C-H alkane               |

SEM images showed porous structure of the chars having pores diameter between 1.95 and 13.4 µm. CM and FM had comparable pore size of 1.95 – 3.76 and 1.49 – 4.95 µm respectively whereas CB had the largest pore size of 2.86 – 13.4 µm. Compared to other biochars produced from woody material (Acacia magnum, Eucalyptus grandis, Gmelina arborea), our biochar (CM, CB, and FM) had more irregular pore size and shape [15]. The relatively low temperature (450°C) and particularly pyrolysis time (90 min) might cause incomplete carbonization process. In spite of poor pore properties, lower temperature pyrolysis was favorable in Pb immobilization because resulting higher available phosphate [23] and increasing available P, K, and Ca associated with effective Pb stabilization [24]. Elemental analysis data from XRF is summarized in Table 4.

Table 4. Elemental % composition of amendments and soil

| Material \ element | O     | K     | Ca    | S     | P     | Si    | Na   |
|-------------------|-------|-------|-------|-------|-------|-------|------|
| CM                | 32.41 | 18.86 | 17.91 | 2.25  | 7.08  | 1.96  | 9.33 |
| CB                | 35.12 | 1.82  | 34.16 | 0.67  | 10.54 | 0.94  | 10.83|
| FM                | 43.33 | 4.30  | 6.82  | 0.97  | 2.63  | 24.70 | 10.19|
| BS                | 43.36 | 2.86  | 7.88  | 2.74  | 2.26  | 19.16 | BDL  |
| C                 | 34.14 | 1.98  | 2.26  | BDL   | 0.74  | 9.04  | 17.74|

Table 4 showed that CM and CB had relatively high mineral content. These minerals had the potential to enrich plant nutrients and increase soil fertility. Si element is prominent for FM and BS as much as 24.70 and 19.16%. The high calcium and phosphorus (Ca and P) content was observed for CM and CB. The values were 17.91 and 7.08% for CM and 34.16 and 10.4% for CB. Chicken manure biochar, CM also had the highest K Content as much as 18.86%. Content of available P, K, and Ca in the amendment was essential in effective Pb stabilization [24]. Because of limitation in instrumental sensitivity, sulfur content in soil control and sodium content in BS were below the detection limit of measurement (BDL). The high content of P in CB and CM confirmed FTIR spectra data at 1046 cm⁻¹ showing phosphate peak.

3.2. Efficacy of amendments in influencing soil-Pb mobility and fraction redistribution

The effect of amendments on soil properties, fraction distribution of Pb, efficacy of immobilization, and risk is summarized in Table 4. Amendments cause changes of soil pH from 5.5 to (6.6 – 8.3) and F1-lead from 17.1 to (3.47–14.72) ppm and induces immobilization efficiency (%) E between 13.92 and 79.71%. Residual fraction (F4) and reducible fraction (F2) also changed significantly but organic fraction (F3) were relatively constant. Residual fraction (F4) changes between 4.69 and 36.23 ppm whereas F2 changes between -3.21 and -34.5 ppm.

The immobilization order is CB > CM > FM > BS. The low cost immobilizing amendments can be applied, either individually or in combination, as phytostabilization agent. The use of amendments
together can provide multi benefits for plants such as decreasing Pb solubility, increasing soil nutrients, and improving physical and biological properties of the soil [20, 25, 26].

All chars rises soil pH and immobilizes Pb. This fact is in good agreement with previous research [10, 20, 23]. In general, chars are more effective than bioslurry. The immobilization order of CB > CM > FM > BS is followed with the increasing trend of F4 and decreasing of F2 and F1 (Figure 3).

**Table 5.** Soil properties, BCR fractions Pb, immobilization efficiency (%E), and risk assessment after incubation with amendments

| Effect AMD | pH | LOI | F1   | F2   | F3  | F4  | F1-4 | E (%) | CF  | RAC | RISK |
|------------|----|-----|------|------|-----|-----|------|-------|-----|-----|------|
| C          | 5.5| 8.78| 17.1 | 69.3 | 11.0| 13.7| 111.1| 0.00  | 7.1 | 15.39 M |
| CM         | 8.0| 9.88| 6.15 | 49.35| 13.04|38.23| 106.8| 64.03 | 1.79| 5.76 L |
| CB         | 8.3| 9.47| 3.47 | 34.8 | 13.0| 49.93| 101.2| 79.71 | 1.03| 3.42 L |
| FM         | 8.3| 9.82| 12.3 | 58.7 | 12.1| 19.5| 102.6| 28.07 | 4.26| 11.99 M |
| BS         | 6.6| 10.48|14.72 |66.09| 10.4|18.39|109.6|13.92 | 4.96| 13.43 M |

Remarks:
- **C**: control soil
- **CM**: chicken manure biochar
- **CB**: chicken bone Biochar
- **FM**: farmyard manure biochar
- **BS**: bioslurry
- **E**: efficiency of immobilization
- **CF = RSP**: Concentration factor; \( CF = (F_1 + F_2 + F_3) / F_4 \)
- **RAC**: Risk assessment code = \%F1.

**Figure 3.** Redistribution of Pb geochemical fraction after amendment

3.3. Environmental risk of Pb after immobilization

Values of contamination factor (CF) and Risk Assessment Code (RAC) are employed to assess the risk. The relationship is: \( CF \leq 1 \) low contamination; \( 1 \leq CF \leq 3 \) moderate contamination; \( 3 \leq CF \leq 6 \)
considerable contamination; and CF > 6 very high contamination [13]. RAC (%F1) expresses risk or mobility of the metal / pollutant and is determined with the proportion of metal in F1 from the total metal concentration in soil. The potential risk is: % RAC < 1 (no risk); 1 < % RAC < 10 (low risk); 10 < % RAC < 30 (moderate risk); 31 < % RAC < 50 (high risk); and % RAC > 50 (very high risk). Table 5 shows that polluted soil has CF and RAC values of 7.1 and 15.39 respectively. It means that the soil has very high Pb-contamination with moderate environmental risk. In this work, CF values of soil after amendment vary from 1.03 to 4.96 and RAC values vary from 3.42 to 13.43%. CB (CF 1.03; RAC 3.42) and CM (CF 1.79; RAC 5.76) were the two most effective immobilizing amendments which remediating soil into low contamination, low environmental risk status.

The changes of environmental risk may be associated with redistribution of lead geochemical fractions during incubation with amendments. Reducible fraction (F2) is dominant in soil before incubation (69.3 ppm). Effective immobilizing amendments (CB & CM) significantly decrease F2, F1 and increase residual fraction (F4). The decrease of F2 is 34.5 and 19.95 ppm while the decrease of F1 is 13.63 and 10.95 ppm for CB & CM respectively. It is, therefore, compensated by the F4 increase of 36.23 and 24.43 ppm.

Toxicity characteristic leaching procedure (TCLP) test is other method in assessing ecological risk of material and waste from USEPA. The test were performed by shaking 1.00 g of soil (material) with 20 mL of 0.1 M acetic acid (solution #2; pH 2.88 ± 0.01) for 16 h in a plastic centrifuge tube [17, 23, 27]. Supernatant was then filtered through quantitative filter paper and measured for leachate concentration. This procedure was very similar to F1 procedure in modified BCR employed in this research work. The only differences were concentration and volume of acetic acid solution; 20 mL of 0.1 M in TCLP versus 40 mL 0.11 M in BCR procedure; hence he result should be comparable. Concentration of acid extractable Pb fraction (F1) of the soil was 17.1 ppm and therefore can be classified as hazardous waste (exceeded regulatory level of 5 ppm). Only CB reduced successfully Pb concentration in acid fraction below critical level; which was 3.47 ppm.

4. Conclusion
FTIR data showed the existence of hydroxyl, carbonyl, C=C, C-H, C-O-C, carbonate, and phosphate groups in the amendments. SEM images showed irregular porous structure of the chars having diameter between 1.95 and 13.4 µm. XRF spectra proved that dominant elements possessed by amendments were Ca, K, Si (for BS & FM), and P (for CB & CM). All amendments immobilized lead in the order of CB > CM > FM > BS. Chicken bone biochar (CB) was the best which immobilized up to 79.71% Pb and might redistribute it from reducible and acid soluble into residual fraction. CB and CM remediated soil from very high contamination-moderate risk into low contamination-low environmental risk status.

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