OPTIMIZATION OF CORN COB BIOCHAR AND TRIPLE SUPERPHOSPHATE FERTILIZER INTEGRATED AMENDMENT TO IMMOBILIZE LEAD (II) IN ACIDIC SANDY SOIL

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Abstract

Elevated levels of Lead (Pb) in soil is due to anthropogenic activities and this could result in highly toxic effects to humans and organisms. Optimization of corn cob biochar (CB) and Triple Superphosphate (TSP) fertilizer integrated amendment for the immobilization of Lead (Pb(II)) was explored for an acidic (pH = 5.50) sandy soil of grain size <2 mm with the following treatments; control, TSP2.5w%, CB2.5w%, CB5.0w%, CB2.5w%+TSP2.5w%, CB5.0w%+TSP2.5w%, CB2.5w%+TSP5.0w%, and CB5.0w%+TSP5.0% were used. The soil was artificially contaminated with 600 mg/kg Pb(II) in the form of Pb(NO₃)₂ and studied according to the Bureau of Reference (BCR) leaching procedure using CH, COOH, NH, OH-HCl, and EDTA. The best immobilization rate of 65% was recorded by the combined corn cob biochar-TSP amendment of ratio 5w%: 2.5w% for the residual fraction and an additional 20% was immobilized by amorphous oxides of Fe(III)/Mn(IV) bound fraction as compared to the TSP and CB separate treatments were immobilization rates were 25% and 45%, respectively in the residual fractions. The phytoavailable Pb concentration decreased to almost half when the combined treatment of TSP and corn cob biochar was used. The point of zero charge measurements (pHpZC≈7.95) indicated corn cob biochar could effectively bind positively charged Pb ions and complexes at pH values of acidic soil system. The combined simultaneous corn cob biochar and TSP treatment proved effective in immobilizing Pb ions. Langmuir isotherm and pseudo-second-order-model (PSOM) better modelled the data, suggesting corn cob biochar adsorption was primarily a monolayer and exhibited chemisorption rate-limiting step respectively.

Keywords: Immobilization capacity; leaching procedure; phytoavailable; Community Bureau of Reference; point of zero charge.

Introduction

Lead (Pb) levels in soil can range from 50 to 400 parts per million, which can occur naturally (Li *et al.*, 2023). However, human activities such as mining, smelting, refining processes, lead-based paint, leaded gasoline, fossil fuels, and industrial facilities

can contribute to the accumulation and contamination of lead in soil. This can lead to elevated lead levels in residential areas, which has become a significant global problem (Anemana *et al.*, 2022; Sun *et al.*, 2019). The accumulation of lead in soil is particularly concerning in mining areas because it is

highly toxic to living organisms and can harm plants (Shi et al., 2021; Delgado et al., 2017). Although studies suggest that the transfer of Pb from soil to plants is not significant, it can accumulate in the human body, especially in bones, leading to harmful health consequences if levels become too high (Darma et al., 2022). Infants and young children are particularly vulnerable, as even small amounts of lead can cause behavioural issues, learning difficulties, and reduced intelligence quotient (IQ). Lead primarily affects the neurological system in children and the cardiovascular system in adults, such as high blood pressure and heart disease (Delgado et al., 2017). Reducing lead contamination in soil requires a combination of physical, chemical, and biological strategies. Biological methods, including phytoremediation, microbial-assisted remediation, and organic improvement remediation, are effective and eco-friendly solutions that are also cost-effective (Dehnavi and Ebrahimipour, 2023). One material that has proven useful in immobilizing toxic metals (TMs) and increasing nutrient levels in contaminated soil is biochar. Biochar enhances soil microbial activities, facilitating the mineralization of organic contaminants. This is due to the organic matter, Nitrogen (N), Phosphorus (P), Potassium (K), Calcium (Ca), Magnesium (Mg), and other nutrients that biochar introduces to the soil, thereby enhancing soil enzyme and microbial activities (Song et al., 2020). Additionally, biochar can increase soil pH and reduce the bioavailability and mobility of soil contaminants. Bashir et al. (2020) and Wang et al. (2020) attribute this to surface complexation, hydrogen bonding, and other mechanisms. However, the effectiveness of soil remediation using biochar depends on factors such as the type of biochar, the nature of contaminants, and soil conditions (Kamali et al., 2022). When using biochar for Pb remediation, the type of biochar, its

preparation conditions, and the level of Pb contamination in the soil are crucial factors to consider. In a certain study, Gao et al. (2022) found that P-loaded biochar produced at 500°C was effective in soil Pb remediation. Chen et al. (2019) suggest that biochar enhances the immobilization of lead (Pb) by reacting with phosphate-solubilizing bacteria (PSB) to form stable hydroxy pyromorphite. In a particular study, the material's ability to immobilize Pb and increase the bioavailability of P in soil was evaluated using an incubation test. The study concluded that activated P-loaded biochar produced at 500 °C provided the best conditions for soil Pb remediation (Acosta-Luque et al., 2022). Furthermore, it was found that biochar application reduced Pb and Cd toxicity by immobilizing these elements in more stable forms and improving soil quality. Biochar and activated carbon were cheap materials suitable for the stabilization of some toxic metals in acidic sandy soils (Ren et al., 2020).

Triple superphosphate, also known monocalcium phosphate monohydrate as [Ca(H₂PO₄)₂.H₂O], has been proven to decrease the bioaccessibility and mobility of lead (Pb) in soil, which reduces the environmental risk associated with lead contamination (Mwilola et al., 2020; Li et al., 2019). The effectiveness of TSP depends on factors such as the application rate, the contact period between TSP and Pb in soil, and other soil properties (Shao et al., 2020; Li et al., 2019). TSP reacts with Pb ions in the soil to form insoluble lead phosphate compounds through a process called precipitation, which reduces the mobility and bioavailability of Pb (Mahamane et al., 2022; Gu et al., 2020). The immobilization process can take time to complete and may vary depending on the specific mechanisms involved (Ren et al., 2019). However, it is difficult to provide a specific timeframe for the immobilization of Pb by TSP in soil (Mamun

et al., 2022). The addition of TSP to soil can increase soil pH and Ca2+ concentration, which enhances the binding reactions between TSP and Pb ions (do Nascimento et al., 2018). In an in-situ remediation study of lead-contaminated soils, TSP was found to be the most effective treatment to reduce Pb bioavailability in soil (Seshadri et al., 2017). The immobilization efficacy of TSP and other phosphate-based materials may vary based on soil properties, Pb concentration, and the type of phosphate material used. TSP immobilizes Pb through an ionic exchange mechanism, releasing phosphate ions (PO₄³⁻) into the soil that can then exchange Pb ions in the soil solution (Sima et al., 2015). This exchange process produces lead phosphate compounds that are less soluble and more stable (Mahamane et al., 2022). Furthermore, the formation of lead phosphate compounds from the reaction between TSP and Pb in soil results in the formation of various lead phosphate compounds (Mahamane et al., 2022), such as pyromorphite and hydroxy pyromorphite, that are less soluble and more stable than soluble forms of Pb, reducing the bioavailability and mobility of Pb. Studies have shown that TSP can be a valuable tool for immobilizing Pb in contaminated soils, as it has the ability to adsorb Pb on its surface, effectively binding Pb ions and preventing them from leaching or being taken up by plants (Sima et al., 2015). The immobilization efficacy of TSP depends on factors such as the application rate, the contact period between TSP and Pb in soil, and other soil properties (Shao et al., 2020; Li et al., 2019). The immobilization capacity of Pb (II) by TSP fertilizer and corn cob biochar integrated amendment in acidic sandy soils has not yet been explored. This goes to answer the impending questions on how corn cob biochar and TSP fertilizer combined amendment can facilitate immobilization and reduction in the phytoavailability of Pb(II) in acidic

sandy soil as we hypothesized that, corn cob biochar and TSP combined amendment can help immobilize Pb(II) in acidic sandy soil. Therefore, the objectives of this study were to investigate the immobilization capacity of Pb (II) in TSP fertilizer and corn cob biochar integrated amendment in acidic sandy soils. Additionally, the study also assessed the effect of TSP fertilizer and corn cob biochar separate and combined amendments to study the phytoavailability fraction of Pb (II) using appropriate soil leaching procedure.

Experimental

Materials and reagents

sample preparation and For dilutions, all solutions were made using analytical grade reagents, and water was distilled and deionized through a Milli-Q® system (Millipore, Billerica, MA, USA). Suprapur quality concentrated ammonia, conc. HNO₂, glacial acetic acid, and conc. HCl from Merck (Darmstadt, Germany) was used. Sigma Aldrich (Germany) provided analytical grade disodium salt of EDTA for phytoavailability (II) nitrate nonahydrate studies. Lead [Pb(NO₃)₂] purchased from Sigma-Aldrich (Germany) was used to prepare the Pb(II) stock solution. Calibration of acidic 1 g/L Pb(II) and In (used as internal standard) stock solutions (Merck) was done after appropriate dilution. All analysis was performed on atomic absorption spectrometry-mass spectrometer (AAS-MS), 200 Series (Agilent AA, Technologies Germany) to determine Pb in the various matrices. BAS-Inc, Tokyo-Japan supplied Ag/AgCl/KCl (saturated), Platinum, glassy carbon electrodes. An electrochemical workstation (Autolab, Eco Chemie, Utrecht, The Netherlands) driven by GPES 4.9 software (Eco Chemie) was also used for quality assurance analysis. Standard solutions were prepared daily from stock solutions through

appropriate dilutions in polypropylene (PP) Falcon® centrifuge tubes (Fisher Scientific, Waltham, MA, USA). An OP-211/2 pH meter (Germany) was used to measure the pH of the leachates. Before sampling, the 50 mL centrifuge tubes were soaked in 20% (v/v) HNO₃ for several days and then rinsed with deionized water.

Preparation of biochar and TSP fertilizer

The corn cobs were collected from the CSIR Crops Research Institute Kwadaso. The corn cob was sort to remove mouldy corn cob and corn cob with soil particles before oven drying until a constant temperature was obtained and cooled to room temperature. The corn cob biochar was pulverized to a size smaller than 2mm and charred in a Nabertherm LT 3/11 Muffle Furnace at 500 °C for 3 hours and then cooled to room temperature. Similarly, TSP fertilizer was obtained from open market in Kumasi, pulverized to a size smaller than 2 mm, and then both amendments were simultaneously added to the Pb-contaminated soil.

Soil incubation treatments

The study was conducted at CSIR Soil Research Institute soil laboratory in Kwadaso, Ghana. High acidic sandy soil samples were collected from the agricultural field of the CSIR Soil Research Institute in Kwadaso which is located at Latitude: 1.6666875 N; Longitude: -1.6666875 W. The soil was sifted to less than 2 mm and treated with TSP obtained from open market in Kumasi, Ghana. The soil texture classification is silt clay loam. The TSP was ground and sifted to less than 53 µm and added to the soil samples at a rate of either 2.5 w% or 5.0 w% for TSP or biochar. The soil was then homogenized by being rotated end-over-end

at 30 rpm. The physicochemical properties of the soil, biochar, and TSP used in the study are listed in Table 1. After homogenizing the soil samples, we took 1 kg of the air-dried acidic sandy soil and placed it in non-perforated polypropylene (PP) round pots that were 30 cm tall and 14 cm in diameter. We then added corresponding amounts of a Pb(II) stock solution, prepared by dissolving [Pb(NO₃)₂] and TSP or biochar, to each soil sample and mixed it thoroughly. The PP pots were then covered with aluminium foil. Additionally, we prepared blank (n=24) and control (n=6) soil samples in triplicate according to the following treatments: Soil sample without either triple superphosphate or corn cob biochar (Control) 2.5w% triple superphosphate (TSP2.5w%), 5.0w% triple superphosphate (TSP5.0w%), CB2.5w%, CB2.5w%, 2.5w% corn cob biochar+2.5w% triple (CB2.5w%+TSP2.5w%), superphosphate 5.0w% corn cob biochar + 2.5w% triple superphosphate (CB5.0w%+TSP2.5w%), corn cob biochar+ 5.0w% triple superphosphate 5.0w% corn cob (CB2.5w%+TSP5.0%), biochar+ 2.5w% triple superphosphate (CB5.0w%+TSP2.5w%). The control soil samples contained only Pb(II) at a concentration of 600 mg/kg. The blank samples contained either soil only, soil with CB, or soil with TSP at two different application rates. For each treatment type, we considered three individual samples. A total of 33 samples underwent additional leaching tests. The study was conducted in a controlled dark place in the laboratory where the temperature was maintained with water at 21 °C, and moisture content was maintained at 65% field water capacity, which was checked weekly for eight weeks. We chose the experimental parameters using a multi-factorial model design (Uzinger et al., 2014).

| Physico-chemical properties and total elements in the amendments used in the study | | | | | |
|--|-------------------|--------------|--------------|--|--|
| Parameter | Acidic sandy soil | Biochar | TSP | | |
| pH | 5.50 1:25v | 12.8 | 7.27 | | |
| Upper limit of plasticity (K _A) | 25.0 | n.a. | n.a. | | |
| Salt content (%) | < 0.02 | n.a. | n.a. | | |
| CEC (meq/100 g) | 5.0 | 24.0 | 5.0 | | |
| TN (%) | 0.18 | 10 | n.a. | | |
| OM (%) | 0.5 | 35.0 | 1.0 | | |
| S (%) | n.a | 0.02 | 2.2 | | |
| P (mg/kg) | 247.39 | n.a. | n.a. | | |
| Ca me/100g | 3.62 | n.a. | 15.0 | | |
| Mg me/100g | 0.64 | 10.0 | n.a | | |
| Clay, <0.002 mm (%) | 4.0 | n.a. | n.a. | | |
| Silt, 0.05–0.002 mm (%) Sand, >0.05 mm (%) | 4.0 92.0 | n.a. n.a. | n.a. n.a. | | |
| Specific surface area | Low | 23.3 | 23.3 | | |
| CaCO ₃ content (%) | Traces | 5.0 | 15.0 | | |
| Metal-binding capacity | Low | n.a | n.a | | |
| Aqua regia soluble Cu (mg/kg) | 4.33 | n.a. | n.a. | | |
| Aqua regia soluble Fe (mg/kg) | 23000 | 900 | n.a. | | |
| Aqua regia soluble Mn (mg/kg) | 225 | 100 | n.a. | | |
| Aqua regia soluble Pb (mg/kg) | 3.85 | n.a | n.a | | |
| | | | | | |

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Abbreviations: CEC = cation-exchange capacity; n.a. = not available; TSP= triple superphosphate

Soil extraction procedures

Modified leaching procedure for BCR soil assessment of the elemental stabilization

To assess the stabilization of elements in the soils studied, a modified soil leaching procedure from the Bureau of Community Reference (BCR) (Rauret *et al.*, 2000), as outlined in Figure 1, was employed. The procedure involved two steps: first, a 0.11 mol/L acetic acid solution was used to extract the water-soluble and carbonaceous fraction, followed by a 0.5 mol/L hydroxylamine hydrochloride solution at pH 2 to extract the fraction bound to amorphous oxides of Fe(III)/ Mn(IV). The ratio of sample mass to extractant volume used in the leaching process was set at 1:40, and the samples were shaken at 30 rpm for 16 hours using an end-over-end shaker from IKA® Works Inc. After centrifugation using a benchtop centrifuge from Hermle Labortechnik GmbH operating at 4500 rpm for 20 minutes, the supernatant was separated from the samples. The total fraction was obtained by MW-assisted digestion of the initial experimental samples in aqua regia (for details, see section 2.4). The BCR Pb stabilization test calculations followed the equation 1:

BCR Pb recovery rate (%) =
$$\frac{\Sigma \text{ fractions of Pb in soil phases}}{\text{pseudototal Pb species in soil}} \cdot 100$$
 (1)

Where: \sum fractions of Pb in Soil phases = Water soluble and carbonaceous Pb fraction + fraction of Pb bound to amorphous oxides of Fe(III)/Mn(IV)+ Pb fraction extracted by aqua regia



Fig. 1: Schematic diagram of the sample preparation steps and analysis performed on the investigated soil samples. Abbreviations: BCR = Community Bureau of Reference, European Commission, ASV= Anodic Stripping Voltammetry and AAS= Atomic Adsorption Spectroscopy

Phytoavailability experiments

In order to estimate the fraction of the sample that is available for plant uptake, we followed the method recommended by Lakanen and Erviö (1971). The ratio of soil mass to the volume of extracting solution was set at 1:10. The soil samples were extracted with a 0.02 mol/L EDTA solution at pH 4.65 for one hour, and the pH was adjusted using concentrated ammonia and an OP-212/2 pH meter (Radelkis Ltd., Budapest, Hungary) followed by centrifugation. To calculate the phytoavailability test for Pb, we used the equation based on the leachate residues obtained from the extraction procedure.

Phytoavailability recovery rate (%) =
$$\frac{\Sigma \text{ fractions of Pb in soil phases}}{\text{pseudototal Pb species in soil}}$$
 • 100 (2)

Where: \sum fractions Pb²⁺ ions in soil phases = Available Pb fraction extracted with EDTA + Pb²⁺ fraction extracted by aqua regia

Microwave (MW)-assisted aqua regia digestion and AAS analysis

To study phytoavailability, the Lakanen and Erviö leaching test was utilized. The process involved extracting dried soil in 40 mL of 0.02 M EDTA solution for 1 hour. The pH was 4.65 and it was measured using an OP-212/2 pH meter from Radelkis Ltd. (Budapest, Hungary). The residues and dried soil were digested in aqua regia by MW-assisted digestion (Fig. 1) according to the procedures described by Lakanen and Erviö (1971) and the modified BCR leaching procedure. This was done to obtain the non-phytoavailable Pb and the immobilized Pb, respectively. These fractions were important for calculating the recovery rates in the different amendments. In summary, 1.0 g of each soil sample was removed from the homogenized samples and transferred to 100 mL PTFE digestion vessels (n = 5). In a 100 mL PTFE digestion vessel, 1.0 g of each dried homogenized soil is measured, followed by the addition of 8.0 mL aqua regia (Fig. 1). The Atomic Adsorption Spectroscopy (AAS) methods used 1% HNO₂, while all the electrochemical analyses were carried out in 0.1M HCl solution.

Studies on the efficacy of corn cob biochar Point of zero Charge Determination on corn cob biochar

The point of zero charge (PZC) for corn cob biochar was determined in 25 mL of 0.001, 0.01, and 0.1 mol/L NaCl solutions using the pH drift method. The samples' pH levels were adjusted between 1 and 12 (n=10) using NaOH or HCl solutions, and the initial pH was recorded. Then, CB was added to the solutions at a rate of 5.0% by weight, similar to soil incubation. The mixtures were equilibrated for 24 hours on an orbital shaker (type TS-2, Turki). After that, the suspensions were filtered through Whatman microfibre glass filters (diameter: 2 mm) using a 12-port Visiprep® solid-phase extraction vacuum manifold (Sigma-Aldrich). The pH of each suspension was measured using an OP-211/2 pH meter (Germany). PZC values were determined by plotting the Δ pH (final pH - initial pH) against the initial pH. The PZC values were obtained by finding the point of intersection of the resulting curve with the abscissa (i.e. at Δ pH = 0), as described by Al-Maliky *et al.* (2021).

Adsorption isotherms and kinetic studies

To study the adsorption of Pb^{2+} , 0.5g/L of corn cob biochar was used. This was agitated gently in a heavy metal solution for 16 hours at room temperature. Samples were shaken for 16 h at 30 rpm using an end-over-end shaker (IKA® Works Inc., Staufen, Germany). After extraction, the supernatant was separated from the samples by centrifugation at 4500 rpm for 15 min performed in a table top centrifuge (Hermle Labortechnik GmbH, Wehingen, Germany) and then the supernatant was collected into a clean tube and topped to the required mark. Finally, microwave (MW)assisted digestion of the leachate residues with aqua regia was applied to obtain the pseudo-total fraction and determined by AAS (for details see also figure 1). The amount of Pb(II) adsorbed by the corn cob biochar was calculated using equation 3:

Adsorption (q) = $\frac{C_o - C_{eq}}{W} \cdot V$ (3)

Where; $q = adsorbed amount of Pb^{2+}$ ions (mg/g), $C_o = initial Pb$ concentration (mg/L), $C_{eq} = Pb^{2+}$ concentration in the adsorption equilibrium (mg/L), V= volume of the solution (L), m = mass of corn cob biochar (g). Each experiment was in triplicates. The removal

efficiency of the biosorbent (corn cob biochar) at equilibrium was determined using Eqn. (4):

Adsorption Efficiency (%) =
$$\frac{C_o - C_{eq}}{C_o} \cdot 100$$
 (4)

where, $C_o = initial$ concentrations (mg/L) $C_{eq} = equilibrium$ concentrations (mg/L) V = volume (L) of the adsorbent W= mass (g) of the adsorbent. The equilibrium adsorption isotherm phenomena were explained by the adsorption isotherms of Langmuir and Freundlich. Langmuir's isotherm (Eqn. 5) is as follows:

$$q_{e} = \frac{q_{max} \cdot K_{L} \cdot C_{n}}{1 + K_{L} \cdot C_{eq}}$$
(5)

Where; $q_{\perp} = \text{maximum}$ adsorption capacity (mg/g), $k_{\perp} = \text{Langmuir's}$ isotherm constant which shows the binding affinity between Pb and corn cob biochar. To identify the adsorption parameters, the transformed linearized form of the Langmuir's isotherm (Eqn. 6) was used.

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_{max}} \cdot \frac{1}{C_{eq}} \cdot \frac{1}{q_{max}} \quad (6)$$

The value of R_L was obtained according to (Eqn. 7)

$$R_{L} = \frac{1}{1 + C_{i} \cdot K_{L}} \qquad (7)$$

Where; R is dimensionless Langmuir constant which indicates adsorption possibility either favourable ($0 < R_L > 1$), unfavourable ($R_L >$ 1), linear (RL = 1) or irreversible ($R_L = 0$). Freundlich's isotherm is represented by (Eqn. 7) whiles the linearized form is shown (Eqn. 8)

$$q_e = K_f \cdot C_e^{\overline{n}} \quad (8)$$

where; K_f is Freundlich's constant which measures adsorption capacity, 1/n represents adsorption intensity which intend indicates the adsorption process either, favourable (0.1

$$\frac{\mathbf{t}}{\mathbf{q}_{t}} = \frac{1}{\mathbf{K}_{2} \cdot \mathbf{q}_{e}2} + \frac{\mathbf{t}}{\mathbf{q}_{e}} \cdot \mathbf{t} \quad (9)$$
$$\log(\mathbf{q}_{e} - \mathbf{q}_{t}) = \log \mathbf{q}_{e} \frac{\mathbf{K}_{1}}{2.303} \cdot \mathbf{t} \quad (10)$$

where $q_t \pmod{g} = \text{amount of adsorption}$ capacity at time $t \pmod{g} = \text{amount of}$ absorption capacity at equilibrium time (min) and k_1 and k_2 = rate constants of the PFOM and PSOM (min⁻¹) respectively.

Additionally, fourier-transform infrared spectroscopy (FTIR) was performed to study the functional groups (Hao *et al.*, 2013) on corn cob biochar and TSP whiles scanning electron microscope (SEM) measurement on the corn cob biochar studied the porosity (Guo *et al.*, 2014).

Statistical analysis

ANOVA was performed by OriginPro 2021b (OriginLab Corporation, Northampton, USA) software for the factorial design verification. Kruskal-Wallis rank-sum test was used to check the violation of assumptions. Var.test and shapiro-Wilk normality were used to check homogeneity and normal distribution respectively. Dunnett's test and Simpson's index were also used to check multiple comparisons of independent samples and concentration accuracies respectively. The vertical error margin of plots was also checked by ErrBars. The R statistical software and DescTools package were used for statistical analysis (Signorell, 2018). The difference between two groups of data was determined using a two-tailed t-test at a significance level of 0.05. Lower-case letters were used in the figures to indicate significant differences between two data groups. If the lower-case

letters of two groups do not contain the same letter, it means that the two groups are significantly different (P < 0.05). If they contain the same letter, it means they are not significantly different (P \ge 0.05).

Results and discussion

Quality assurance of Pb determination

To ensure the accuracy of the results, we compared concentration data from AAS-MS and ASV-MS analytical techniques for soil treatment combinations. Due to the electrode's sensitivity to organic matter, which could foul the electrode surface and hence the results. the leached samples were subjected to the highest dilution factors (Yantasee et al., 2008) to ensure that RSD values were as low as possible (<10%). The results of both analytical techniques for relevant sample matrices were compared and found to be in good agreement (as shown in Table 2). The BCR sequential extraction procedure was used to estimate the water-soluble and carbonate fraction of Pb, using two of the five leaching steps, specifically acetic acid and hydroxylamine hydrochloride (Tong et al., 2020). The easily reducible fraction due to binding to amorphous Fe(III) and Mn(IV) oxides was determined (Anemana, 2020). It ensured the quality of our results by accounting for sample variability when analyzing soil chemical samples (Sharma et al., 2022). The AAS-MS analytical instrument was highly effective in determining Pb in soil with good detection limits and dynamic range, eliminating impurities arising from the sample leaching/digestion process (Van Loon, 1983). Throughout the study, care was taken to ensure close attention to procedural blanks, precision, recovery, and accuracy of results. It thoroughly investigated all potential blank combinations and found no significant detectable levels of Pb in the blank samples, allowing us to establish accurate mass

balances and determine the distribution of Pb between different leachate fractions. Precise measurements were performed on individual leachate samples (Table 2) and discovered an average deviation of $\pm 7\%$. Samples were tested in triplicate to ensure accuracy. Our findings revealed that the average pseudototal concentration of Pb was 599.9 \pm 0.61 mg/kg, which was almost identical to the nominal value of 600 mg/kg Pb. In the lower concentration treatment, the minimum and maximum values had a difference of approximately 7% from the nominal value (refer to Table 3 for more information). To determine recovery by using equations 1 and 2, the concentration of Pb in different leachates to the pseudototal Pb concentration (Söderberg *et al.*, 2019) were compared (Table 3). We expected that the total concentration in the different fractions would be lower than the corresponding pseudototal concentration, and our results confirmed this. However, with a few exceptions, the difference did not exceed 4% (refer to Table 3). The sum of the Pb concentration in the different fractions was either slightly lower or higher than the corresponding pseudototal

concentration, but the deviation did not exceed 17%. Considering the complex nature of soil system, these deviations between the two analytical instruments confirm the accuracy of the results as stated by Anemana, 2020.

| | <i>oy</i> 1110 1110 <i>unu</i> 1 | 1.57 | | |
|-----------------------------|----------------------------------|-----------------------|---------------|--|
| | | Analytical techniques | | |
| +600mg/kg Pb (II) treatment | Sample matrix | Concentration (mg/ | $kg \pm SD$ | |
| | * | AAS | ASV | |
| + Control | AcOH leachate | 300 ± 4.4 | 303±5.1 | |
| + TSP2.5w% | NH ₂ OH leachate | 120 ± 2.8 | 115±3.0 | |
| + TSP5.0w% | pseudo-total | 603.0 ± 8.1 | 601±9.0 | |
| + CB2.5w% | AcOH leachate | 240 ± 3.8 | 244±2.9 | |
| + CB5.0w% | EDTA leachate | 84 ± 2.5 | 88 ± 3.0 | |
| +CB2.5w%+TSP2.5w% | NH ₂ OH leachate | 120 ± 18 | 124±16 | |
| +CB5w%+TSP2.5w% | EDŤA leachate | 78 ± 3.2 | 85±4.3 | |
| + CB2.5w%+TSP5w% | ΣEDTA fractions | 605.4 ± 9.6 | 598±8.8 | |
| +CB5w%+TSP5w% | pseudo-total | 600.5 ± 8.1 | 606 ± 7.9 | |

| TABLE 2 |
|---|
| Total Pb concentrations $(n = 3)$ in relevant soil sample matrices determined |
| by AAS-MS and ASV |

Abbreviations: CB-Corn cob biochar, TSP-triple superphosphate, w%-Weight percentage, AcOH-Acetic acid, AAS-atomic absorption spectroscopy, ASV-anodic stripping voltammetry

TABLE 3

Total Pb concentration (n = 3) for the relevant soil treatments compared to the sum of the concentrations in various leachate fractions.

| | Leaching test | t Concentration (mg/kg \pm SD | | |
|-----------------------------------|---|---------------------------------|---|--------------|
| Soil treated with 600 mg/kg Pb in | - | Pseudo total | Σ fractions | Recovery (%) |
| + Control | fit-to-purpose BCR phytoavailable Pb | 588.0±1.4 | $605.1{\pm}0.2$ $580.0{\pm}0.1$ | 102 99 |
| + TSP2.5w% | fit-to-purpose BCR phytoavailable Pb | 601.0 ± 0.7 | $\begin{array}{c} 603.6 \pm 0.2 \\ 596.0 \pm 0.4 \end{array}$ | 104 99 |
| + TSP5.0w% | fit-to-purpose BCR phytoavailable Pb | 603.0 ± 1.1 | $\begin{array}{c} 620.2\pm 0.5 \\ 605.1\pm 0.1 \end{array}$ | 103 100 |
| + CB2.5w% | fit-to-purpose BCR phytoavailable Pb | 586.5 ± 0.2 | $\begin{array}{c} 605.1 \pm 0.1 \\ 570.0 \pm 0.6 \end{array}$ | 103 97 |
| + CB5.0w% | fit-to-purpose BCR phytoavailable Pb | 600.0 ± 1.7 | $\begin{array}{c} 602.3 \pm 1.7 \\ 606.5 \pm 0.2 \end{array}$ | 100 101 |
| +CB2.5w%+TSP2.5w% | fit-to-purpose BCR phytoavailable Pb | 611.5 ± 0.1 | $\begin{array}{c} 604.5 \pm 0.1 \\ 606.1 \pm 0.6 \end{array}$ | 99 99 |
| +CB5w%+TSP2.5w% | fit-to-purpose BCR phytoavailable Pb | 608.0 ± 0.1 | $\begin{array}{c} 583.0 \pm 0.1 \\ 596.0 \pm 0.6 \end{array}$ | 97 98 |
| + CB2.5w%+TSP5w% | fit-to-purpose BCR phytoavailable Pb | 600.5 ± 0.1 | $\begin{array}{c} 604.5 \pm 0.1 \\ 605.4 \pm 0.6 \end{array}$ | 101 101 |
| +CB5w%+TSP5w% | fit-to-purpose BCR phytoavailable Pb | 600.5 ± 0.1 | $\begin{array}{c} 604.5 \pm 0.1 \\ 605.4 \pm 0.6 \end{array}$ | 101 101 |

Total Pb and Pb concentration (n=3) for the relevant soil treatments compared to the sum of the concentrations in the various leachate fractions. *CB* = Biochar; w%= weight of corn cob biochar Triple superphosphate fertilizer; BCR =Community Bureau of Reference

FTIR spectroscopy analysis

Infrared spectroscopy is a process used to analyze the different functional groups in lignin, cellulose, and hemicellulose. To begin, the crystal plate of the IR spectrometer is cleaned thoroughly to ensure that there are no interfering peaks (Yang *et al.*, 2007). A background spectrum is taken before the sample is placed on the crystal plate to be scanned. Then, the reference sample is scanned twenty to four times from 200 to 4000 nm⁻¹ wavenumber to obtain the spectrum for the sample. In this study, FTIR was used to observe the chemical changes of corn cob biochar before and after Pb adsorption (Fig. 2a). The intensity profiles of corn cobs before and after Pb adsorption were different, especially at wave numbers 3300cm⁻¹, 2038cm⁻¹, 1560cm⁻¹, 1300cm⁻¹, 1050cm⁻¹, and 748cm⁻¹. These values correspond to O-H, C=C, C-O, and C-H stretching vibrations. By analyzing the subtracted spectra of corn cob biochar loaded with Pb, changes in the spectra were observed. The broad peak at 3300 cm⁻¹ was attributed to the stretching of the hydroxyl group (O-H) and H bonding in polymeric compounds with alcohol and phenol in CB. This was responsible for the intermolecular hydrogen bonding of Pb and functional groups of biochar such as alcohols, phenols, and carboxylic acids. The weak peaks of C=O stretching observed at 2038 cm-1 and C-O stretching observed at 1050 cm⁻¹ could be attributed to C-OH groups. However, despite the large BET surface area, the adsorption capacity of corn cob biochar is significantly low due to the lack of chemical activation (Hao et al., 2013). Therefore, the idea of extending the immobilization studies with TSP fertilizer was developed. The bands observed in the FTIR spectra are assigned to [PO₄³⁻] Hap tetrahedral apatite structure, [PO₄³⁻]], Asymmetric, symmetric deformation modes PO₄ group O-P-O bending vibrations, HPO₄²⁻ PO₄, PO₂, C-O, esters/phenols/alcohols, CO_3 , deformation vibrations of water, PO_4), OH, and OH bonds (Fig. 2b). These bands correspond to low concentration of HPO²⁻. The functional groups of TSP responsible for Pb immobilization are anionic groups such as carboxyl, amine, and hydroxyl (George, & Wan, 2023). When added to soil, TSP can react with Pb to form insoluble Pb phosphate minerals such as pyromorphite (Chrysochoou, Dermatas, & Grubb, 2007). Immobilization of Pb can also occur by precipitation, adsorption, and ionic exchange reactions (Zheng et al., 2017). Others such as goat manure, lime, and phosphate can also stabilize exogenous Pb in soils, with phosphate having a better passivating effect than alkaline materials (Zhao et al., 2021).



| ince bands | Assignment | | |
|-------------------|---|---|--|
| m ⁻¹) | | | |
| 748 | С—Н | Alkene | |
| 1050 | СН | Alkene | |
| 1300 | С—Н | Alkene | |
| 1560 | С—О | Alcohol & Phenol | |
| 2038 | C=C | Alkyne | |
| 3300 | 0—Н | Alcohol & | |
| | nce bands m ⁻¹) 748 1050 1300 1560 2038 3300 | nce bands Assignment m ⁻¹) 748 C—H 1050 C—H 1300 C—H 1560 C—O 2038 C=C 3300 O—H | |



| Absorbance bands (cm ⁻¹) | | Assignment |
|--------------------------------------|---------|--|
| a | 480.10 | $_{V2}(PO_4^{3-})$ Hap tetrahedral apatite structure |
| b | 543.33 | $_{\rm V4}({\rm PO}_4^{-3-})$ |
| с | 566.63 | |
| d | 601.81 | Assymetric, symmetric |
| f | 665.56 | deformation modes (P0 ₄) V ₂ group (O-P-O) bending vibrations |
| h | 857.56 | v(OH) |
| i | 952.73 | $Vas(P(0H)_2)$ |
| 0 | 1078.41 | $Vas(PO_2)$ |
| m | 1232.95 | _v C-O, esters/phenols/alcohols |
| k | 1454.32 | $(CO_3) V_2$ |
| j | 1650.04 | $_{\rm V1}(0{\rm H})$ deformation vibration of ${\rm H_20}$ |
| v | 2051.63 | |
| р | 2165.01 | $(\mathbf{r}\mathbf{O}_4)\mathbf{v}_3$ |
| u | 2320.00 | |
| n | 2924.42 | v(UII) |
| t | 3460.15 | $_{V_3}$ (OH) bonds matching low concentration of HPO ₄ ²⁻ |

Figure 2. ATR-FT-IR spectra of vibrational bands of corn cob biochar before and after Pb(II) adsorption (a) and the functional groups of TSP fertilizer (b). Alphabets represent vibration bands

Adsorption studies

The researchers conducted batch adsorption experiments to find the best way to use the adsorbent. They used both the single-layer Langmuir adsorption and multilayer Freundlich isotherms to evaluate the adsorbent's capacity to retain and remove contaminants and to comprehend how these contaminants interact with the adsorbent surface (Saadi *et al.*, 2015). The Langmuir model required a plot of the inverse of the equilibrium adsorption uptake as opposed to the inverse of the equilibrium concentration, while the Freundlich isotherm required a plot of $\text{Log}(q_e)$ versus $\text{Log}(C_e)$ (Ragadhita, & Nandiyanto, 2021). The data demonstrated a good fit with the Langmuir isotherm (Fig. 3a), which showed a favourable adsorption possibility of R_L, compared to the Freundlich isotherm (Fig. 3b).



Fig. 3: Lead adsorption studies according to Langmuir (a), Freundlich (b), pseudo-first-order (c) and pseudosecond-order (d) adsorption isotherms and kinetic models.

The maximum adsorption capacity was 78.24726 mg/g (Table 4), and the Langmuir isotherm better modeled the data, suggesting that the corn cob biochar adsorption was primarily on a monolayer which was similar to the study by Vu *et al.*, 2017 which employed the use of modified corncob-biochar and the data on pesticide removal by Alsherbeny *et al.*, 2022 best fitted the Langmuir isotherm. The adsorption kinetic studies indicated that the removal of Pb²⁺ by the corn cob biochar adsorbent was evaluated using the pseudo-first-order and pseudo-second-order kinetic models. The PSOM model was the most appropriate kinetic model, with an R² value of

0.9332

0.99998 (Fig. 3d) as compared to fig. 3c (Table 4), suggesting that chemisorption is the ratelimiting step. Ho *et al.*, 2001 also utilized the second-order kinetics sorption of lead (II) on peat. By considering the amount of absorption capacity at equilibrium time (min) by corn cob, biochar is an efficient adsorbent for removing Pb^{2+} species.

| | | | TABLE 4 | ļ | | | |
|---|---------------|-------------------------|------------------|---------------------|-----------------------------|--------------------------------------|----------------|
| | Adso | orption isotherm i | nodels for Pb | $^{2+}$ by the corn | a cob biochar | | |
| | | Pseudo-firs | st-order kine | tic | Pseudo-second-order kinetic | | |
| | | $q_e (meq g^{-1})$ | $k_1 (min^{-1})$ | \mathbb{R}^2 | $q_e (meq g^{-1})$ | k ₂ (g mg ⁻¹ m | nin^{-1} |
| Pb (II) | q_Exp. (mg/g) | . 4082 0.00 | 0(0(210 | 22.5250 | R ² | 0.0000 | |
| | 23.60 | 0.4082 -0.00 | 06 0.6310 | 23.5350 | 0.3195 | 0.9999 | |
| | | | | | | | |
| | | | TABLE 5 | | | | |
| Kinetic adsorption models for Pb^{2+} by the corn cob biochar | | | | | | | |
| Langmuir model | | | Freun | dlich model | | | |
| Pb (II) | K | q _{max} (mg/g) | R _L R | 2 | K _r | 1/n | R ² |

0.9994

0.4098

Point of zero charge and corn cob biochar surface analysis

78.2473

0.0288

The pH level increases as the pyrolysis temperature increases. This is due to the separation of alkali salts from organic materials, loss of acidic functional groups, and the appearance of basic functional groups (Domingues *et al.*, 2017; Tag *et al.*, 2016). In a study by Oginni *et al.* (2020), the pH levels of wood biomass from longleaf pine, red oak, and hard maple increased after pyrolysis at 500°C. The values were 8.6, 9.0, and 9.8, respectively.



4.3692

0.5349

Fig. 4: Point of zero charge for the corn cob biochar prepared at $500^{\circ}C$

The charge point of corn cob biochar refers to the pH level at which the surface of the biochar is electrically neutral. This affects its ability to adsorb or release ions and contaminants under different environmental conditions. To measure the biochar from corn cobs prepared at 500°C, the mass titration (MT) method was used, as described by Al-Maliky et al. (2021). The pHpzc versus equilibrium pH dependence can indicate the charge of particles in the aquatic system. Low pHpzc indicates the dominance of negatively charged anionic groups on the material surface (Assirey & Altamimi, 2021). The point of zero charge (pHpzc) of corn cob biochar varies depending on the specific conditions and methods used to produce and measure it. Usually, it falls within the range of pH 2-8.1. In this study, the pHpzc was found to be 7.95 (Fig. 4). This indicates that the surface of the corn cob biochar is positively charged. When pHpzc > 7.95, it gives the biochar the capability to adsorb the positively charged Pb ions, thus leading to Pb immobilization.

Figure 5 shows the BET analysis is a technique used to examine the surface area and pore volume of biochar. It involves measuring the volume of nitrogen gas (N₂) absorbed and desorbed. In this particular study, the biochar prepared at a temperature of 500°C had a specific surface area of 585.81 m² g⁻¹ and a pore volume of 0.33 cm³ g⁻¹. These results were similar to those obtained from corn cobs. The BET technique also estimated the adsorption mean pore diameter to be 1.58 nm (Guo *et al.*, 2014). The porous biochar had a rough texture, which provided a large specific surface area.



Fig. 5: Scanning electron microscopy images of the surface at $2000 \times$ magnification showing the surface area and pores of the corn cob-derived biochar at 20 kV.

The micrographs and BET results indicated that corn cob biochars prepared by the in-house pyrolysis technique were an excellent structure for a low-cost and environmentally friendly adsorbent without chemical modification. The BET technique is commonly used to estimate the specific surface area from adsorption isotherms. For corn cob biochar, the specific surface area was 655.79 m² g⁻¹, and the pore volume was 0.26 cm³ g^{-1} , indicating its porosity similar to a study by Genovese et al., 2015, which recorded a BET-specific surface area of 543.7 m² g⁻¹. However, it is worth noting that the porosity of corn cob biochar is affected by various pyrolysis conditions, such as temperature and heating rate. The biochar has a mesoporous structure, with estimated adsorption mean pore diameter of 1.58 nm using the BET technique

(Guo *et al.*, 2014). While the adsorption capacity of corn cob biochar is low without chemical activation, other factors such as functional group, acid/base character, pore type on the biochar surface, carbonisation

temperatures, and activations may influence Pb²⁺ immobilization (Campos *et al.*, 2020).

3.6. Application of a fit-to-purpose BCR extraction procedure for the evaluation of Pb immobilization in TSP and or corn cob biochar-amended acidic soil



Fig. 6: Lead distribution (%) among the fractions obtained after performing fit-to-purpose BCR leaching (a) and phytoavailability (b) tests. Error bars represent the relative standard deviation (%) of the calculated data (n = 3). Abbreviations: TSP = triple superphosphate, %w= percentage weight, AcOH acetic acid, and CB = corn cob biochar.

Previous studies have shown that the application of P-compounds in soil can result in acidification, which may increase the mobilization of metals, including Pb (Sherman et al., 2006). However, when P-materials are added to soil, they can cause the formation of Pb phosphates and convert Pb minerals into insoluble chloropyromorphite (Miretzky, & Fernandez-Cirelli, 2008). In this study, different rates of TSP and corn cob biochar were added to soil samples, either alone or in combination, to determine their effectiveness in immobilizing Pb. The results showed that the combined treatment of TSP and CB had the highest Pb immobilization rate, with TSP 5.0w% + CB 2.5w% being the most effective among the combined treatments. It was found that 17% of total Pb in the acidic sandy soil was naturally immobilized, while 35% was immobilized by the carbonaceous fraction and 48% of the 600 mg/kg $[Pb(NO_2)_2]$ was recorded for the acetic acid leachate. This indicated that there was limited interaction between the metal ions and biochar resulting in the solubilization of Pb(II) ions (Rizwan et al., 2021). When TSP or CB was used alone, CB had a slight advantage of about 10% due to the prevention of solubilization. The efficacy of TSP at 2.5w% and 5.0w% application rates was similar, and doubling the application rate of CB from 2.5w% to 5.0w% resulted in a 5% increase in immobilization rate, which was also comparable to TSP2.5w%+CB2.5w%. However, CB2.5w%+TSP2.5w% in the

treatment, Pb^{2+} mobilization occurred probably due to acidification by TSP addition. The treatments TSP5.0w%+CB2.5w%, TSP2.5w%+CB5w%, and TSP5.0w% +CB5.0w% (Fig. 6a) showed comparable results, indicating the efficacy of the combined treatment with corn cob biochar and TSP.

Overall, approximately 63% of Pb2+ was immobilized in the acidic sandy soil system. The TSP and CB addition possibly stabilized complexation, Pb(II) through binding, precipitation, or cation exchange sites (Xu et al., 2021). The pH of the acidic soil used was 5.5, and the environmentally relevant PZC value of the CB was at pH \approx 7.95, which supports this finding. The pH values can significantly affect the distribution of metal species in soils, as demonstrated by Pukalchik et al. (2018). In the amendment where corn cob was combined with TSP, significant immobilization of Pb occurred, up to about 60% to 62% compared to 15% in the control soil system. The hydroxylamine hydrochloride leachate fraction of the amended soil system recorded a much more significant difference in Pb mobilization compared to the control soil. This is presumably due to the binding of Pb to the amorphous Fe (III)/Mn (IV) oxide fraction due to the higher CEC in the biochar and the higher CaCO₂ content of the TSP. Similar phenomena occurred with the remediation of Cd in soil (Zhang et al., 2024; Li et al., 2020). The immobilization capacity of Pb could be attributed to amorphous oxides of Fe(III)/ Mn(IV). The direct adsorption mechanism could somewhat enhance the direct substitution of Ca²⁺ (in P-compounds) by metal cations Pb²⁺ as shown in equation 11 (Zeng et al., 2017).

$$Ca_{10}(PO_4)_6(OH)_2 + xM^{2+} \longrightarrow (M_x, Ca_{10,x})(PO_4)_6(OH)_2 + xCa^{2+} (11)$$

direct adsorption

The TSP compound has a unique ability to release phosphate ions, which can replace Pb ions in the soil. This exchange process leads to the formation of lead phosphate compounds that are less soluble and more stable. When TSP and biochar are added together to the soil, it results in an increase in pH, ionic attraction through functional groups, CEC, and the formation of new minerals (Marcińczyk et al., 2022) such as pyromorphite [Pb_s(PO₄),Cl], hydroxy pyromorphite [Pb₅(PO₄)₃(OH)], Pb phosphate $[Pb_2(PO_4)_2]$, and Pb hydrogen phosphate (Zeng et al., 2017). These minerals are less soluble and more stable than the soluble thereby reducing the bioavailability and mobility of Pb. The TSP treatment showed a higher immobilization capacity of about 35%. The immobilization rate of corn cob biochar was double that of the immobilization rate of the TSP amendment. However, the immobilization rate reached 65% when the combined TSPbiochar treatment was applied to 600 mg/kg Pb(II) contaminated acidic soil. The untreated contaminated soil (reference soil) sample immobilized about 15% Pb(II) (Anemana, 2020). This was similar to the study for multiple heavy metals immobilization (Wang et al., 2018). The recommended application rate of biochar to arable land is between 1.0% and 5.0% (Shen et al., 2024; Anemana et al., 2019). The selection of 2.5 w% and 5.0 w% application rates for corn cob biochar and TSP was made to compare the results of these additional amendments, assuming that biochar and TSP complement each other to achieve a better immobilization rate (Lwin et al., 2018). When both corn cob biochar and TSP were applied proportionally and simultaneously, the immobilization of the Pb(II) dose increased almost proportionally (Li, & Gao, 2019). An application rate of 5.0 w% each of TSP and corn cob biochar amendment slightly mobilized Pb < 10%, suggesting that either 5.0 w%: 2.5 w% biochar: TSP or 2.5 w%: 5.0 w% biochar: TSP application rates were the most effective with optimal results. The study found

that the combined TSP and biochar amendment reduced BCR leachability and bioaccessibility of Pb with a maximum reduction of about 67%. The decrease of exchangeable and carbonatebound Pb fractions was observed, while the residual Pb fraction was increased (Huang *et al.*, 2016), indicating that the Pb in soils was transferred to a more stable fraction with the application of the CB and TSP.

3.7. Assessment of phytoavailability of Pb (II) in artificially contaminated acidic soil with TSP and or Corn cob biochar amendment by using EDTA extraction

EDTA is a chelating agent commonly used to stabilize and dissolve metal ions. It is known that plants can absorb nutrients by acidifying the root surface accompanied by a reduction in H^+ (Anemana *et al.*, 2019). Leaching with hydroxylamine can help estimate the phytoavailable fraction of Pb, hence, the distribution of Pb in hydroxylamine hydrochloride and EDTA leachates showed similarities (Luo et al., 2018). EDTA releases Pb by interacting directly with other metal ions through complexation, which is similar to the reduction of amorphous Fe(III)/Mn(IV) minerals (Kim, 1996). The phytoavailable Pb fraction estimated by leaching with EDTA was found to be about 30% of the total Pb in the reference soil (Fig. 6b). The immobilization rate recorded was 10% with TSP 2.5 w%, TSP 5.0 w%, or CB 2.5 w% amendments as compared to the controls. The mobilization rate for CB 5.0 w% was approximately 14% compared to TSP 5.0 w% + CB 2.5 w%. This indicates that the optimal immobilization of Pb²⁺ in the amended soil can be achieved through a combination of 2.5 w% TSP amendment with either 2.5 w% or 5.0 w% corn cob biochar (Fig. 6b).

Distribution of Fe(mg/kg) and Mn(mg/ kg) in Fe (III)/Mn(IV) amorphous oxides in hydroxylamine hydrochloride leachates amended with CB and TSP



Fig.7: Fraction of Pb (mg/kg) bound to amorphous oxides of the Fe(III)/Mn(IV) after BCR and phytoavailability leaching tests(a). Distribution of Fe(mg/kg) and Mn(mg/kg) in Fe(III)/Mn(IV) amorphous oxides in hydroxylamine hydrochloride leachates (b). Values with the same letter(s) are not significantly different (ANOVA, P < 0.05). Error bars represent the relative standard deviation (%) of the calculated data (n = 3). Abbreviations: TSP = triple superphosphate, %w= percentage weight and CB = corn cob biochar.

The levels of both iron (Fe) and manganese (Mn) are crucial in binding and solubilizing lead (Pb^{2+}) in the amorphous manganese and iron oxides. The treatment of CB 2.5w%+TSP2.5w% showed the highest leaching of Fe, ranging from 4100-4750mg/kg, which was comparable to CB 5w%+TSP2.5w% and CB 5w%+TSP5w%. This suggests that the TSP corn cob biochar has added Fe into the treatments. The lowest concentrations of Fe were recorded with TSP amendment, which was consistent with the

preliminary Fe analysis in the soil, TSP, and CB. It was also assumed that some of the Fe in the soil was bound to the chemical functional groups of the TSP and could not be solubilized easily (Li & Gao, 2019; Bolan et al., 2014). The leachates showed the concentration of Mn ranged from 24 to 38mg/kg. The TSP treatments recorded the lowest Mn concentration, while the CB-treated soil sample recorded the highest Mn concentration, comparable to the TSP corn cob treatment. These concentrations of Mn in the leachates agreed with a study by Yusof et al., 2009. Phosphorus compounds can also promote the adsorption of Pb on iron (hydr)oxides in the soil, thus increasing the amorphous iron oxide (AFeO) fraction as highlighted by (Zeng et al. 2017). Pb is known to strongly bind to iron (hydr)oxides, hence increasing Pb adsorption onto iron (hydr) oxides is vital for Pb remediation in soils or sediments (Shi et al., 2021). Additionally, Pb can be adsorbed to goethite by forming inner-sphere surface complexes with the surface hydroxyl groups (≡FeOH). Another mechanism for Pb adsorption could follow the surface complexation model in equations 13-15.

| \equiv FeOH + Pb ²⁺ = \equiv FeOPb ⁺ + H ⁺ | 13 |
|---|----|
| \equiv FeOH + Pb ²⁺ = \equiv FeOHPb ²⁺ | 14 |
| $\equiv FeOH + Pb^{2+} + H_2O = \equiv FeOHPb^{2+}$ | 15 |

In this study, the average deviation of Pb in hydroxylamine hydrochloride and EDTA leachates was less than 4.6% indicating similarities between hydroxylamine hydrochloride and EDTA (Anemana *et al.*, 2019; Gismera *et al.*, 2004).

Conclusions

Lead-contaminated soil continues to pose as a serious health risk to humans, animals, and the ecosystem on a global scale. Therefore, it is imperative to explore cheap, readily available, sustainable, and environmentally friendly technologies to ameliorate this problem. Both the biochar and TSP complemented each other in terms of the higher porosity, higher pH values and many functional groups which are very important in Pb (II) immobilization. The study involved the following treatments: TSP2.5w%, TSP5.0w%, CB2.5w%, CB2.5w%, CB2.5w%+TSP2.5w%, CB5.0w%+TSP2.5w%, CB2.5w%+TSP5.0%, and CB5.0w%+TSP5.0w%. However, the optimization application rate of corn cob biochar and TSP in the ratio 5.0w%: 2.5w% immobilized the highest Pb(II) concentration in the acidic sandy soil system. Similar results were also obtained for the phytoavailability studies where 5.0w% each of corn cob biochar and TSP fertilizer in a combined treatment recorded the lowest Pb(II) mobilization rate which was significantly lower than in TSP or corn cob biochar mobilization rates in the contaminated soil system. The combined corn cob-TSP treatment in the acidic contaminated soil system proved superior. However, further research is needed on calcareous soil systems and soils with more complex matrices. The study was carried out in experimental pots in laboratory setting which limits its generation especially in on field experimentation.

Credit author statement

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Conflicts of interest

The authors declare no conflict of interest.

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