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Treatment of clay soil contaminated with lead by in-situ immobilization process using animal bones

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Abstract

In this work, the application of bone wastes –Cow Bone, Pig Bone, and Horse Bone for the treatment of Lead (Pb) in Clay Soil by in-situ immobilization process, was investigated. The bone wastes were carbonized at a temperature of 700 OC for five hours. The Cow Bone Ash (CBA), Pig Bone Ash (PBA), and Horse Bone Ash (HBA) obtained were characterized with X-Ray Fluorescence (XRF). The physicochemical analysis of the soil sample was also performed. Batch experiments were done to investigate the effects of amendment dosage, time, and pH on immobilization efficiency. The physicochemical characterization of the amendments showed that they contain principally calcium phosphate. The XRF revealed that CBA contains 49.25 % CaO and 42.406 % P_2O_5, PBA contains 46.6 % CaO and 40.488 % P_2O_5 and HBA contains 45.664 % CaO and 33.857 % P_2O_5. The batch immobilization experiment revealed that CBA performed better than other sorbents in the removal of Pb. The removal efficiency is in the order CBA > PBA > HBA. The maximum removal of Pb in 100 g of soil was 71.2 %. This investigation has shown that animal bones can successfully remediate lead by immobilization process in a Pb contaminated Clay soil.

Keywords: Immobilization; Animal Bones; Lead; Clay soil; In-situ

1. Introduction

The contamination of soil by heavy metals has been on the increase for the past few decades due to the increased world population, urbanization, industrialization, and intensified agricultural activities. Lead is one of the most common heavy metal pollutants listed by the Environmental Protection Agency (EPA) [1, 2].

Lead is a metal with atomic number 82, atomic mass 207.2 g, density 11.4 gcm^{-3}, melting point 327.4^{o}C, and boiling point 1725 ^{o}C It belong to group IV and period 6 of the periodic table. It is a naturally occurring, blue-grey metal usually found as a mineral combined with other elements, such as (PbS, $PbSO_4$), or oxygen ($PbCO_3$) and ranges from 10 to 30 mg/kg in the earth crust [3]. Typically mean lead concentration for surface soil averages 32 mg/kg and ranges from 10 to 67 mg/kg [4].

Lead is used for the manufacture of lead storage batteries, soldering purposes, manufacture of bearings, electric cable covers, production of ammunitions, plumbing, pigments and caulking [2].

In spite of the above importance of Lead, it has the following detrimental effects to Man: It accumulates in the brain leading to poisoning or even death. It also affects the gastrointestinal tract, kidney, and central nervous system. Children exposed to lead are at risk of impaired development, lower intelligence quotient (IQ), shortened life span, hyperactivity and mental detoration. In adults lead exposure results in loss of memory, nausea, insomnia, anorexia and weakness of, the joints [5, 2].

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The general forms in which Lead are released into the soil, ground water and surface waters are in form of ionic lead, Lead (II) oxides and hydroxides and lead metal oxyanion complexes. The most stable forms of Pb are Lead (II) and Lead-hydroxyl complexes. Pb (II) is the most common and reactive form of lead. Lead (II) compounds are ionic (e.g. Pb^{2+}, $SO4^{2-}$), whereas Pb (IV) compounds such as tetraethyl lead $Pb(C_2H_5)4$ tend to be covalent. Lead also forms several basic sacks such as Pb $(OH)_2$. $2PbCO_3$ which was then used as a white pigment in paints. This was the source of chronic lead poison to children who ate peeling white paint. In addition to the inorganic compounds of lead, lead poisoning also emanates from organic compounds such as tetraethyl lead which was a gasoline additive [6].

The following ways have been suggested for removing Pb from contaminated soils: excavation and Landfilling, soil washing, soil flushing, electro kinetic process, phytoremediation, and stabilization/solidification [2]. The major problem with the above strategies is that separation and removal take a long time and energy [6]. [7] Pointed out that an economical and effective method of remediation of soils contaminated by heavy metals is in-situ immobilization by the use of inorganic and organic amendments. Some of the organic materials that have been used not only to immobilize heavy metals but have also improved soil fertility. Some of these materials include bark, chitosan, zeolite, clay, fly ash, rice bran, and peat moss [8]. Cow bone ash is the partly carbonized remains of Cow bone. It consists of mainly calcium and phosphorous. It helps the soil by increasing its alkalinity and also provides organic nutrients to the soil. Cow Bone Ash, Pig Bone Ash and Horse Bone Ash contain functional groups such as Alkynes, ketones, oxides and hydroxides of phenols, aromatic phosphate and aldehydes. These functional groups make it a good adsorbent by forming a covalent bond with the soil constituents.

In this work, cow bone, pig bone, and horse bone ash – wastes that cause environmental problems are utilized in reducing the lead mobility in the soil by forming precipitates when it reacts with organic matter and oxide/hydroxide forming complexes like lead carbonates, orthophosphates and pyromorphites. These complexes are insoluble and therefore reduce their mobility by making it less available to plants that are consumed by animals [9].

2. Materials and methods

The Clay soil was collected from Amagunze. Lat. 6.382541 and Long. 7.486532 in Nkanu East Local Government Area of Enugu State, Nigeria. Cow bone and Pig bone were collected from Oye Emene Central Abattoir in Enugu East LGA while the Horse bone was from Obollo- Afor main market in Udenu local Government Area of Enugu State. The bone samples were prepared according to the method described by [10]. The bones were washed with water severally, cut into pieces with a cutlass, and rewashed again repeatedly to remove impurities on the surface. They were rinsed with de-ionized water and transferred to the oven at 80^oC to dry. The dried bones were crushed in a motorized crusher and transferred to a furnace where they were ignited at 700^oC for five (5) hours. The samples were characterized with X-Ray Fluorescence (XRF) and Atomic Absorption Spectrometer (AAS) to determine the mineral composition and heavy metal content respectively.

2.1. Physicochemical Analysis of the Soil Samples

The soil sample was classified by the method of sieve analysis. The pH was determined using British standard [11]. A wet oxidation method by Walkley black [12] was used in the measurement of soil organic matter. CEC was determined according to the procedure of [13]. The phosphate content of the soil was determined by the method of [14]. The Nitrogen content of the soil was determined following the method of [15]-modified kjeldahl. The potassium content of the soil was obtained following the method [16]. Iron oxide in the soil sample was determined following the method described by [17].

2.2. Spiking of the Soil with the Heavy Metal lead

The soil was spiked following the method described by [18]. 1kg of soil and 3g of amendments were ground in a wood plate with grinding rod. The material was sieved with 2 mm sieve. The mass of the metal species leads II Nitrate (Pb $(NO_3)_2$, was added. The whole mass was placed in polyethylene bags and shaken thoroughly. The experiment was repeated with 5g of the amendments.

2.3. Incubation Experiment

The soil sample and the amendments were incubated following the method described by [19, 20]

100g of air-dried contaminated soils were mixed thoroughly with various amendments at a specific application rate on a dry basis in a 500ml. The three amendments – Cow Bone Ash (CBA), Horse Bone Ash (HBA), and Pig Bone Ash (PBA) were applied in the soil. 25ml $NaNO_3$ was added as background electrolyte. The water content of the soil was adjusted to 65% water holding capacity by adding deionized water with the aid of a pipette. Throughout the experiment deionized water was added to compensate the water losses. The containers were placed in the open air to mimic a natural condition. The samples were taken during different periods of incubation for 2, 7, 14, 30, 60, 150, and 300 days. The soil pots were thoroughly mixed during the incubation process. At each time the percentage immobilized was obtained, based on DTPA- Extractable fraction as follows:

$$\% \, Immobilized = \left(\frac{CO - Ct}{Co}\right)100 \qquad (1)$$

Where

- Co= Initial metal conc. in mg/kg
- Ct = concentration of metal at time t (mg/kg).

The available heavy metal in the soil was extracted in DTPA (Diethylene-triamine- penta-acetic acid) as described by [21].

The DTPA- TEA solution was prepared by mixing 0. 01 $mol.L^{-1}CaCl_2$, 0.005 $molL^{-1}$ DTPA and 0.1 Tri-ethanolamine (TEA) at pH adjusted to 7.3. $1mol.l^{-1}$.Hcl solution was used in adjusting the pH. 10g of the soil samples (0.15mm) were weighed into a 500ml. Erlenmeyer flask, 20mls of DTPA-TEA extracting solution was added and shaken for 2 hours. The soil suspension was centrifuged at 2000 rpm for 15 minutes and allowed to stay for 1 hour. The clear supernatant was diluted to 50 ml with distilled water [18]. The DTPA- extractable content were determined with AAS model AA340N

3. Results

3.1. Physicochemical Properties of the Soil

Some selected physicochemical properties of the soil used in this research are presented in table 2.1.

Table 1 Physiochemical properties of the soil

parameter	**Sand (%)**	**Silt (%)**	**Clay (%)**	**pH**	**OM %**	**EC S/m**	**CEC meq/100g**	**P_2O_5 meq/100g**	**Moisture %**
	33.20 %	5.60 %	60.20 %	6.45	31.74	1228.40	6.22	1.12	42.30 %
Parameter	**Cadmium**	**Chromium**	**Lead**	**Fe_2O_3**	**Al_2O_3**				
	0.02 mg/kg	0.01 mg/kg	0.30 mg/kg	0.65 meq/100g	0.21 meq/100g				

OM=Organic Matter, EC= Electrical conductivity, CEC= Cation exchange capacity.

The texture of the soil was clay. The soil texture plays an important role in the mobility of metals in soils. Texture reflects the particle size distribution of the soil clay and mineral oxides. These compounds are important adsorption media for heavy metals in the soil [27]. The pH of the soil is 6.45. In general, metal sorption increases with increasing pH. That is, the lower the pH value the more metals can be found in the solution and thus more metal is mobilized. The pH of the soil sample was acidic and hence will favor desorption or mobility. The mobility of heavy metals was increased by lowering pH [27]. The organic content of the studied clay soil is very high as can be seen in Table 1. Organic matter is important for the retention of metals by soil solids as it decreases mobility and bioavailability. However, even though the organic matter in the soil favors the retention of heavy metal but excess of it increases solubility of metals due to complexation reaction of heavy metals [27].

The phosphate content of the soil is 1.12 (meq/100g) and therefore classified as low phosphate soils. Generally, anions such as sulfate can coordinate metal ions to form insoluble complexes. [9] had shown that phosphate rock primarily flu apatite (Ca10¬ (P04)6 Fe) effectively immobilized Lead from 39% to 100%. The content of lead (Pb) is very low when compared to the regulatory standards of 200 mg/kg [7].

3.2. Chemical Properties of the Bone Samples.

Selected properties of the animal bones used for the immobilization study are shown in table 2.

Table 2 Chemical Properties of the bone samples

Parameter	**Bone samples**			
	Units	**CBA**	**HBA**	**PBA**
Total carbon (TC)	%	17.80	16.76	20.92
Phosphate (P_2O5)	%	42.406	33.857	40.488
Calcium oxide (CaO)	%	49.295	45.664	46.467
Cadmium (Cd)	mg/kg	0.01	0.02	0.03
Chromium (Cr)	Mg/kg	0.001	0.001	0.02
Lead (Pb)	Mg/kg	0.05	0.07	0.06
Calcium (Ca)	%	51.09	30.32	33.27

Total carbon (TC) of the bone sample ranges from 16.76% to 20.92% with pig bone the highest. The high values of the total carbon of the three bone samples as shown in table 4 is an indication that they are all effective immobilization agents.

The bone samples contain high percentages of calcium and phosphate, with the cow bone having the highest concentration followed by the pig bone and the least is the Horse bone.

The high quantity of calcium phosphate explains the basic mechanism of immobilization of heavy metal with animal bones.

The composition of the bone samples show that it is an appetite family with hydroxyapatite (Ca5 (P04)3 0H (HA), the lead member of large class of substituted compounds of similar structure [28].

The basic mechanism is dissolution which results in ion exchange and this is followed by precipitation. The formation of pyromorphite, an insoluble compound depends on the availability of soluble metal and phosphorus [29].

From table 2, it was observed that the values obtained for concentration of heavy metals Pb, Cr and Cd were all within the permissible limit for WHO/FAO and E.U standards. Lead in the bone sample is (0.05mg/kg). This is far below the WHO/FAO and EO standards of 0.3mg/kg each.

Table 3 XRF Analysis of CBA

Element	**Concentration %**	**Peak(cps/mA)**
Fe_2O_3	0.14225	442
SiO_2	0%	
Al_2O_3	1.572	1151
MgO	3.380	614
P_2O_5	42.406	82076
SO_3	0.6399	1563
Na_2O	1.839	124
Cao	47.035	97230

Table 4 XRF Analysis of PBA

Element	Concentration %	Peak(cps/mA)
Fe_2O_3	0.15621	486
SiO_2	10	0
Al_2O_3	1.392	1019
MgO	3.394	617
P_2O_5	40.488	78355
SO_3	0.9065	2215
Na_2O	1.586	106
TiO_2	(0.00009)	0
MnO	0.01700	219
CaO	46.467	97124
K_2O	0.7238	935

Table 5 XRF Analysis of HBA

Element	Concentration %	Peak(cps/mA)
Fe_2O_3	0.6628	2060
SiO_2	0.589	569
Al_2O_3	1.441	1055
MgO	3.486	633
P_2O_5	33.857	65523
SO_3	1.0953	2676
Na_2O	3.663	248
TiO_2	0.00581	23
MnO	0.05052	652
Cao	44.124	97180

The XRF analysis of CBA, PBA and HBA represented in Tables 3, 4 and 5 respectively show that the bone samples are principally made up of calcium phosphate. The quantity of the compound increases in the order CBA > PBA > HBA as shown in Tables 3-5.

3.3 Analysis of the Batch Incubation Experiment

The immobilization of Lead (Pb) by animal bone amendments – Cow Bone Ash (CBA), Pig Bone Ash (PBA) and Horse Bone Ash (HBA) are presented in fig 1. The amendment was added to the soil in two levels of 3% and 5% while the control is one without any amendments.

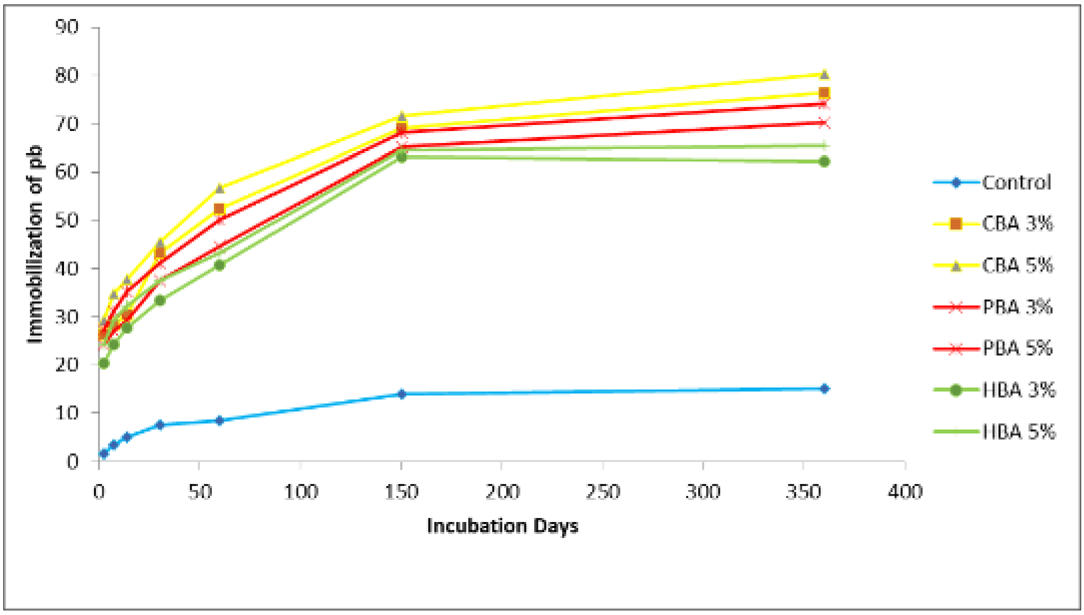

Figure 1 Immobilization of pb in Clay Soil

From the figure 1, the percentage immobilization increased with the incubation period. In the control, the immobilization increased from 1.5 % to 14.01 % for a period of 150 days and only 1 % from 150 to 360 days.

The natural attenuation will do little to reduce the concentration of heavy metals as can be seen in the Control Experiment [30], but with the CBA amendment in the soil the concentration of the heavy metal have been reduced from 2000.58 mg/kg to 496 mg/kg with application rate of 3% and to 393.9 mg/kg with an application rate of 5 % representing 76.54 % and 86.32 % of immobilization respectively after 360 days.

PBA with 3% application rate reduced the concentration of the heavy metal (Pb) in the soil to 595.95 mg/kg after 360 days and with 5 % application rate it reduced to 520.13 mg/kg representing 70.26% and 74.04 % immobilization respectively. With 3% HBA, the concentration of Pb in the soil was reduced from 2000.53 mg/kg to 753.0 mg/kg and with 5 % HBA it was reduced to 634.17 mg/kg after 360 days incubation representing 63.36 % and 68.3 % immobilization respectively.

The mechanism of lead immobilization could be dissolution and precipitation of hydroxyl pyromorphite which is insoluble, these processes are represented in equations (1) and (2). [31] Pointed out that metal immobilization can also take place through cation exchange mechanism of Pb2x ion substituted by Ca2x ion in solution following reaction of equation (2), complexation and surface coating.

$$Ca10\ (P04)6\ (0H)2x\ X\ Pb2x \rightarrow Ca10\text{-}x\ Pbx\ P04\ (0H)2 + X\ Ca2x \qquad (2)$$

4. Conclusion

Comparative analysis of data in this investigation showed that Cow Bone Ash (CBA), Pig Bone Ash (PBA) and Horse Bone Ash (HBA) can be used to immobilize and thus remediate Clay soil contaminated with Pb, The XRF analysis of Cow Bone Ash, Pig Bone Ash and Horse Bone Ash showed that they contain high percentage of calcium and phosphorous oxide minerals which aids dissolution and precipitation of insoluble hydroxyl pyromophyte The incubation experiment revealed that the highest percentage immobilization was obtained with CBA, followed by PBA and then HBA.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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