

An Optimization Study of the Attenuation of Lead in a Contaminated Clay Soil by In-situ Immobilization Process Using Waste Animal Bones

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Abstract— In this research animal bones a waste product were used as low-cost amendments for the removal of metal ions such as Lead II ions from soil. Some of the soil and bone physicochemical characteristic was determined using XRF. The effects of immobilization time, dosage and PH were evaluated. The optimum condition for the remediation of lead was determined using Design expert version 8.0. The physicochemical characteristics of the soil reveals that the soil contains high moisture and organic matter thus making it a high retainer and immobilization of metals. The physicochemical characteristics shows that the bone samples contain mainly calcium phosphate which promotes immobilization by complexation, adsorption and desorption processes. The optimum Pb removal in Clay Soil using CBA, are time of 141 days, pH of 8.1 and dosage of 5.3g with the predicted percentage immobilization of 71.22%. With PBA, the optimum conditions are pH of 8.0, dosage of 5g and time of 150 days and the predicated percentage immobilization of 68.55% and with HBA, the optimum conditions are; pH of 7.77, dosage of 4.74g and time of 170 days and the predicted percentage immobilization of 64.91%.

Keywords— Immobilization, lead, optimization, waste bones.

I. INTRODUCTION

In-situ immobilization of heavy metals in contaminated soils have been adjudged as the most economic, convenient and fastest remediation strategy [1,2] Lead is used for the manufacture of lead storage batteries, for soldering purposes, for the manufacture of bearings, as electric cable covers, in the production of ammunitions, in plumbing, pigments, jewelry, ceramic glazes, toys, stainless glass and caulking [3] The major sources of chronic lead poison to children is by eating peelings of 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. [4] Other sources of lead poison to children most especially could emanate from imported toys tainted with lead. The lead could be in the paint and even in the plastic itself. Children get in contact with lead by chewing on the toy. [3] Lead poison also do arise from drinking water as a result of the use of pipes that are made of lead and brass or even as a result of the fact that some plumbers still use lead solder to join copper pipes. The health effect of lead poisoning cannot be over emphasized, at a high levels of exposure, lead attacks the brain and central nervous system to cause coma, convulsions and even death. Even after surviving severe lead poisoning, children may develop behavioral issues

and mental disability. Lead exposure at lower levels can impact a child's brain development, leading to a low intelligence quotient (IQ), behavioral abnormalities such decreased attention span and increased antisocial behavior, and a decline in scholastic achievement. In addition, anemia, hypertension, renal impairment, and reproductive organ damage are caused by lead exposure [4].

Soil amendments such as manure, compost, bio- char, clay minerals, phosphate compounds coal fly ash, and liming materials have been widely used as immobilizing agents for potentially toxic elements because of their abilities to restrain PTEs through different mechanisms [5,6] Other organic amendments that have been used to immobilize lead include: Cow manure, Mussel shell powder, Cow bone powder, Oyster shell, Egg Shell, Chicken bone, Poultry manure ,Oak wood, Vegetable waste, Wood bark, Dead pig derived biochar, Soybean Stover biochar, Rice straw, Wheat [7] Some liming materials have been added to the soil to raise the pH. These materials have been found to immobilize potential toxic elements by several mechanisms such as adsorption and desorption, complexation, precipitation and ion exchange. Due to the alkaline nature, these materials reduce H⁺ concentration, thereby increasing negatively charged sites in the soil. Consequently, positively charged potentially toxic elements can be sorbed onto negative sites [8] The toxic elements will also precipitate in the form of carbonates, hydroxides, phosphates and oxides thereby lowering its mobility [6] Phosphates containing amendments such as appetites, hydroxyl appetites, diammonium phosphates (DAP), phosphates-based salts, phosphoric acid, and phosphate rocks (PR) have successfully been used to immobilize potentially toxic elements in contaminated soils [9]. The immobilization of Lead by phosphate-based amendment is effective due to the formation of stable lead phosphates, such as pyromorphite which precipitates forming insoluble compounds [10]. [11] Pointed out that phosphate amendments significantly reduced lead immobilization through formation of chloropyromorphite Pb₁₀{PO₄}₆Cl₂ and Fluor pyromorphite (Pb₁₀{PO₄}₆F₂).

From the foregoing, it is evident that there are a lot of literature on the use of organic materials for the immobilization of Pb in contaminated soil but there are few information on the application of the amendments for optimum immobilization efficiency. In this work, Cow Bone Ash (CBA), Pig Bone Ash

(PBA) and Horse Bone Ash (HBA) were used to optimize the efficiency of immobilization.

II. 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 [12]. The bones were washed with water severally, cut into pieces with a cutlass and rewashed again repeatedly to remove impurities on the surface. The bones were rinsed with de-ionized water and transferred to the oven at 80°C to dry. The dried bones were crushed in a motorized crusher and transferred to a furnace where they were ignited at 700°C for five (5) hours. The samples were characterized with XRF and AAS to determine functional groups, morphology, mineral composition and heavy metal content respectively.

Physicochemical Analysis of the Soil Samples

The soil sample was classified by the method of sieve analysis. The pH was determined using British standard [13]. A wet oxidation method by Walkley black [14] was used in the measurement of soil organic matter. CEC was determined according to the procedure of [15]. The phosphate content of the soil was determined by the method of [16]. The Nitrogen content of the soil was determined following the method of modified kjeldahl method [17]. The potassium content of the soil was obtained following the method described by [18] and the iron oxide determined following the method described by [19].

Spiking of the Soil with the Heavy Metals

The soil was spiked following the method described by [2]. 1kg of soil and 3g of amendments were ground in a wood plate with grinding rod. the material is sieved with 2mm sieve. the mass of the metal species leads ii nitrate (pb (no3)2), was added. the whole mass was placed in a polyethylene bags and shaken thoroughly. the experiment was repeated with 5g of the amendments.

Optimization Studies

The heavy metal immobilization process was optimized using response surface methodology. This is a method capable of depicting second order or higher other models [20]. This was done in order to determine the best condition for optimum immobilization of metals by the amendments. The factors considered were time, dosage, and pH, these factors were the independent variables whereas the percentages of the heavy metals immobilized and stabilized were the dependent variables or responses. In this work, a set of 20 experiments were performed for each of the three amendments, identified as Cow Bone Ash (CBA), Pig Bone Ash (PBA) and Horse Bone Ash (HBA). The experiments for the optimization of the immobilization of the metals by the amendments were conducted using the experimental conditions as shown in Table 1. The responses obtained from various runs are significantly different which implies that the factors have effects on the response

TABLE 1: Experimental Design Matrix with Three Variables

Std	Run	Factor 1 A: pH	Factor 2 B: Dosage (g)	Factor 3 C: Time (day)
1	1	6	3	50
19	2	8	5	150
15	3	8	5	150
6	4	10	3	250
16	5	8	5	150
7	6	6	7	250
9	7	6	5	150
14	8	8	5	250
3	9	6	7	50
20	10	8	5	150
2	11	10	3	50
12	12	8	7	150
4	13	10	7	50
8	14	10	7	250
17	15	8	5	150
5	16	6	3	250
13	17	8	5	50
11	18	8	3	150
18	19	8	5	150
10	20	10	5	150

III. RESULTS AND DISCUSSIONS

Physicochemical Properties of the Soil

Some selected physicochemical properties of the soil used in this research are presented in table 2.

TABLE 2: Selected physiochemical properties of the soils.

parameter	Sand(%)	Silt(%)	Clay%	pH	OM	EC S/m	CEC meq/100g	P2O5 meq/100g	Moisture
	32%	5.60%	60.20%	6.45	31.74	1228.40	6.22	1.12	42.30 %
parameter			Lead	Fe2o3	Al2o3				
			0.30 mg/kg	0.65 meq/100g	0.21 meq/100g				

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 [21].

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 solution and thus more metal is mobilized [21]. 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 [21].

The organic content of the studied clay soil is very high as can be seen in Table 2. Organic matter is a key parameter for metal sorption and desorption [21]. The preservation of metals

by soil solids, which lowers their mobility and bioavailability, is facilitated by organic matter. Nevertheless, while an excess of organic matter in the soil helps to retain heavy metals, the complexation reaction of the metals makes an excess of it more soluble [21].

The phosphate content of the three soils ranges from 0.98 (meq/100g). They are therefore classified as low phosphate soils. Generally, anions such as sulphate can coordinate metal ions to form insoluble complexes. [23] have 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. [18].

Chemical Properties of the Bone Samples

Selected properties of the animal bones used for the immobilization study are shown in table 3.

TABLE 3: Selected Chemical Properties of the bone samples

Parameter	Units	Bone samples		
		CBA	HBA	PBA
Total carbon (TC)	%	17.80	16.76	20.92
Phosphate (P ₂ O ₅)	%	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. According [12], in his study of the preparation and characterization of activated cow bone powder for the adsorption of cadmium from palm oil mill effluent pointed out that carbon surface influenced sorption and the hydro apatite arrangement of the phosphate ion and provided sites for the attraction of cadmium ions.

TABLE 4: RSM Results for the immobilization of Metals in Clay soil using Cow Bone Ash(CBA), Pig Bone ASH (PBA), and Horse Bone Ash (HBA)

Std	Run	Factor 1 A: pH	Factor 2 B: Dosage G	Factor 3 C: Time day	PBA Percentage Pd Immobilized (%)	CBA Percentage Pd Immobilized (%)	HBA Percentage Pd Immobilized (%)
1	1	6	3	50	22.25	24.33	24.24
19	2	8	5	150	68.80	71.36	65.2
15	3	8	5	150	68.80	71.36	65.2
6	4	10	3	250	57.41	60.18	54.97
16	5	8	5	150	68.80	71.36	65.2
7	6	6	7	250	57.07	60.55	54.13
9	7	6	5	150	60.22	63.72	56.01
14	8	8	5	250	66.42	70.24	64.23
3	9	6	7	50	41.12	44.36	36.41
20	10	8	5	150	68.50	71.36	65.2
2	11	10	3	50	45.36	48.48	41.13
12	12	8	7	150	58.17	62.73	62.02
4	13	10	7	50	40.35	43.30	43.12
8	14	10	7	250	62.43	65.16	60.15
17	15	8	5	150	68.80	71.36	65.2
5	16	6	3	250	40.16	43.36	36.33
13	17	8	5	50	50.70	54.10	47.23
11	18	8	3	150	61.20	64.72	56.5
18	19	8	5	150	68.80	71.36	65.2
10	20	10	5	150	67.11	70.07	61.16

The high values of the Total carbon of the three bone samples as shown in table 3 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 OH (HA), the lead member of large class of substituted compounds of similar structure [24].

The basic mechanism is dissolution which results in ion exchange and this is followed by precipitation. [22] The formation of pyromorphite, an insoluble compound depends on the availability of soluble metal and phosphorus. [25].

From table 3, it was observed that the values obtained for concentration Pb, is 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.

XRF Analysis Result

X-ray fluorescence tube analysis was used to determine the quality and types of mineral oxides in the sample. The results for CBA, PBA and HBA respectively show that the samples mainly contain oxides of calcium and phosphorous. CBA has 46.47% CaO and 40.49% P₂O₅ while HBA has 45.66% CaO and 33.90% P₂O₅. CBA, HBA and PBA contain calcium phosphate. They are able to immobilize heavy metals because the phosphates they contain dissolves mineral that results in insoluble phase. [17].

RSM results for the immobilization processes.

ANOVA Analysis, Model Fitting and (3-D) Response Surface Plots

ANOVA for immobilization of Pb in Clay Soil using CBA, PBA and HBA shows an F value of 43.43, 41.96 and 40.56 respectively. Their P-values are less than 0.0500 indicating significance with the terms A, B, C, AB, A², B², and C². The model equations are given below

$$\text{Percentage Pb immobilized from Clay Soil using CBA} = +71.56 + 5.09A + 3.50B + 8.49C - 4.68AB + - 4.96 A^2 - 8.13 B^2 - 9.68 C^2 \quad (1)$$

$$\text{Percentage Pb immobilized from Clay Soil using PBA} = +68.55 + 5.18A + 3.28B + 8.37C - 4.47AB - 4.59A^2 - 8.57B^2 - 9.70C^2 \quad (2)$$

$$\text{Percentage Pb immobilized from Clay Soil using HBA} = +65.11 + 5.34A + 4.27B + 7.77C - 2.85AB - 6.38A^2 - 5.71B^2 - 9.24C^2 \quad (3)$$

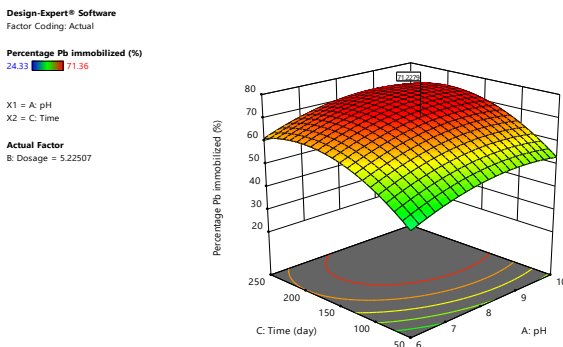


Fig. 1: Response Surface plots for Fig the effect of Time and pH on the immobilization of Pb from Clay soil by CBA

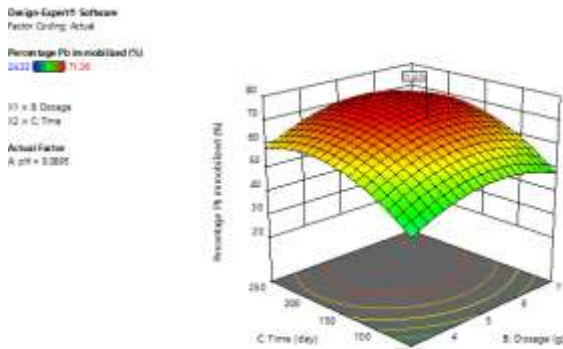


Fig. 2: Response Surface plots for the effect of Time and Dosage on the immobilization of Pb from Clay soil by CBA.

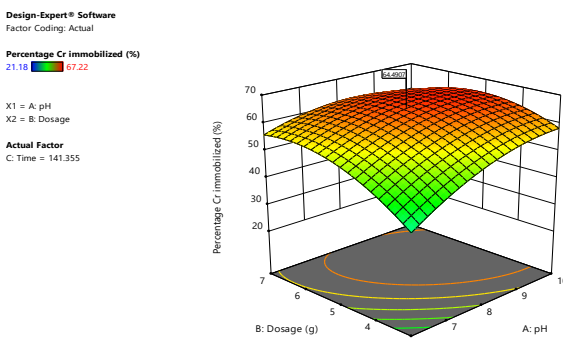


Fig. 3: Response Surface plots for the effect of Dosage and pH on the immobilization of Cr from Clay soil by CBA

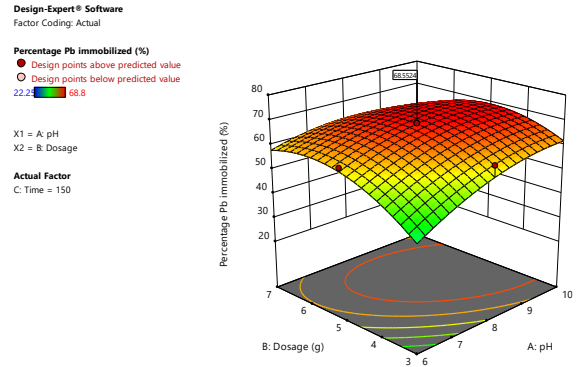


Fig. 4: Response Surface plots for the effect of Dosage and pH on the immobilization of Pb from Clay soil by PBA

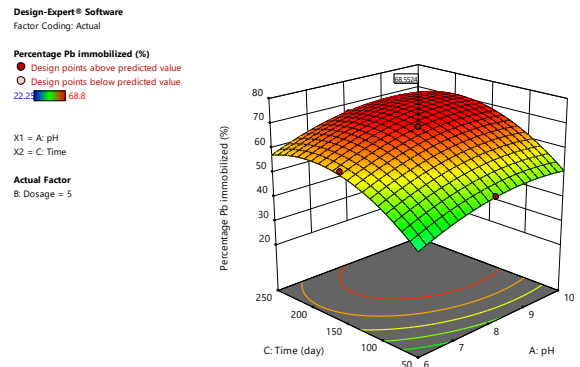


Fig. 5: Response Surface plots for the effect of Time and pH on the immobilization of Pb from Clay soil by PBA

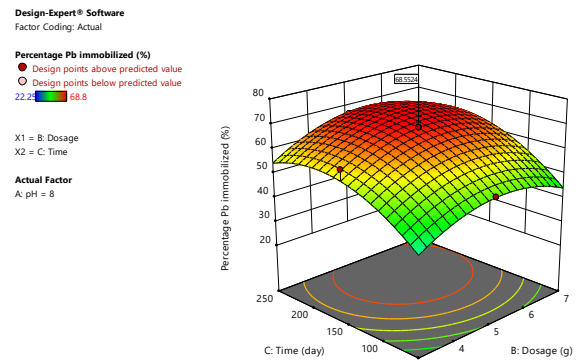


Fig. 6: Response Surface plots for the effect of Time and Dosage on the immobilization of Pb from Clay soil by PBA

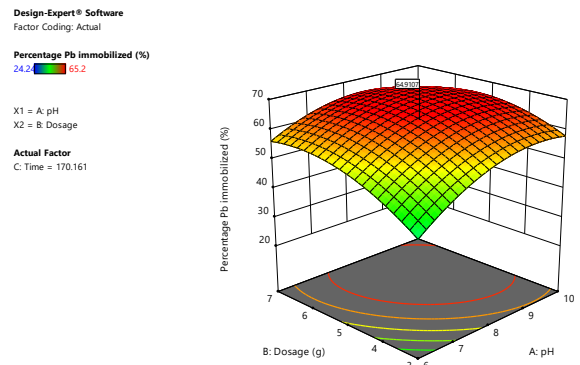


Fig. 7: Response Surface plots for the effect of Dosage and pH on the immobilization of Pb from Clay soil by HBA

Design-Expert® Software
Factor Coding: Actual
Percentage Pb immobilized (%)
24.2 65.2
X1 = A: pH
X2 = C: Time
Actual Factor
B: Dosage = 4.74314

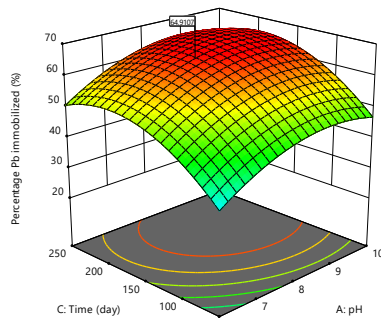


Fig. 8: Response Surface plots for the effect of Time and pH on the immobilization of Pb from Clay soil by HBA

Design-Expert® Software
Factor Coding: Actual
Percentage Pb immobilized (%)
24.2 65.2
X1 = B: Dosage
X2 = C: Time
Actual Factor
A: pH = 7.77749

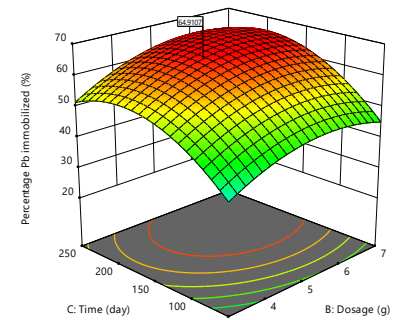


Fig. 9: Response Surface plots for the effect of Time and Dosage on the immobilization of Pb from Clay soil by HBA

TABLE 5: Validation of the Optimization Result

Experiment	Optimum Results			Predicted Valued	Experimented	% Deviation
	pH	Dosage (g)	Time(hrs)	Mg/kg	Mg/kg	
Immobilization of Pb in clay soil by CBA	8.099	5.220	141.355	71.227	71.024	0.00275
Immobilization of Pb in clay soil by PBA	8.0	5.0	150	68.52	68.35	.0025
Immobilization of Pb in clay soil by HBA	7.77	4.74	170.16	64.91	64.73	0.0028

IV. 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, Sandy soil and Lateritic 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. Surface morphological analysis of CBA, PBA and HBA using scanning electron microscope (SEM) revealed existence of large and high concentration of calcium, carbon and phosphorus atoms. FTIR analysis of the animal bones shows that they consist mainly of hydroxyl groups, ethylene group and aromatic phosphates. Statistical analysis of data revealed the following/conditions: The optimum immobilization of Pb with CBA, is at a time of 141 days, pH of 8.1 and dosage of 5.3g and the predicted immobilization of 71.22%. With PBA is at a pH of 8.0, dosage of 5g and time of 150 days and the predicated percentage immobilization of 68.55%. and with HBA, it is at a pH of 7.77, dosage of 4.74g and time of 170 days and the predicted percentage immobilization of 64.91% thus the increasing order is CHA > PBA > CBA.

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