



## Kinetics of Lead Immobilization in Clay Soil Using Animal Bones

Eze, Kenneth Afamefuna

Department of Chemical Engineering, Enugu State University of Science and Technology, Agbani

### ABSTRACT

In order to immobilize lead (Pb) in clay soil, researchers looked into using bone debris from cows, pigs, and horses. For four hours, the bone byproducts were carbonized at a temperature of 700 °C. The CBA, PBA, and HBA that were collected from cows, pigs, and horses were each given a unique description. Clay Soil, according to the physicochemical study, By running the experimental data through different kinetic models—including simple Elovich, parabolic diffusion, power function, pseudo-second order, and pseudo-first order—the kinetics of metal sorption and desorption were studied. The amendments are mainly composed of calcium phosphate, according to their physicochemical characteristics. In terms of calcium and phosphorus concentration, CBA is higher than PBA, which is higher than HBA. When tested against other sorbents in a batch immobilization experiment, CBA removed more lead from clay soil. According to the kinetic analysis, desorption of metals followed the Elovich model, whereas the sorption of all other metals followed the second order model.

### Introduction

Lead, a bluish-gray metal that occurs naturally, is typically found in minerals with other elements like sulfur (PbS, PbSO<sub>4</sub>) or oxygen (PbCO<sub>3</sub>) and has a concentration in the earth's crust ranging from 10 to 30 mg/kg (Loissi et al., 2017). Lead storage batteries, bearings, soldering, electric wire covers, ammunition, and pigments are among its many uses (Wuana and Okieimen, 2011). It is used in the production of high-quality products by alloying with other metals. Some examples of these products include lead-antimony batteries, lead-strontium-silver anodes, lead-tin-antimony sleeve bearings, lead-and-tellurium pipes and sheets for chemical installations, and lead-and-tellurium nuclear shielding. As said by Manahan in 2003.

Lead ions, lead (II) oxides and hydroxides, and lead metal ox anion complexes are the most common forms of lead that seep into groundwater, surface waters, and soil (GWR TAC 1997). Lead sulfide (PbS), the most stable solid form, precipitates out of the soil matrix at pH levels greater than 6, along with other insoluble lead compounds such lead phosphate and lead carbonates.

Lead (IV) compounds, like tetraethyl lead Pb (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, are more likely to be covalent than lead (II) compounds, which are ionic (e.g., Pb<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>). One of lead's many basic molecules is 2PbCO<sub>3</sub>, which was often a white pigment in paintings. Another is Pb(OH)<sub>2</sub>. For kids who snacked on peeling white paint, this meant a steady diet of lead poisoning.

Lead poisoning impacts many bodily systems, including the kidneys, the brain, the central nervous system, the gastrointestinal tract, and the red blood cells. Children that are exposed to lead may experience developmental delays, a decreased IQ, attention deficit hyperactivity disorder (ADHD), and mental decline. Reduced reaction time, memory loss, nausea, sleeplessness, anorexia, and joint weakness are some of the symptoms of lead exposure in adults. (Khan et al., 2012; Wuana and Okieimen 2011; Khan et al., 2008).

The adsorption rate, process modeling, and information prediction regarding the adsorbent/adsorbate interaction (physio sorption or chemisorption) can be achieved by fitting the experimental data into several kinetic models. The source is Amanda et al. (2013). This study examined the sorption and desorption processes of lead in clay soil to determine the rate of lead immobilization. According to Hashema and El-khiraig (2013) and Priyantha and Bandaranayaka (2011), two models were utilized to model the sorption process: pseudo-first-order and pseudo-second order.

The pseudo-first-order rate equation for liquid solid adsorption system is expressed as follows:

$$\frac{dx}{dt} = k(X - x) \quad (1)$$

Where X and x (mg/g) are the adsorption capacities at equilibrium and at time t respectively. (Xu et al., 2008) K and unit (min<sup>-1</sup>) is the rate constant of pseudo-first order reaction. On linearization, the equation becomes

$$\log(q_n - q_i) = \log(q_m) = \frac{-K}{2.303}t \quad (2)$$

$$\text{or } \ln(q_m - q_i) = \ln q_m - Kt \quad (3)$$

Where q<sub>m</sub> = adsorption capacity at equilibrium mg/g, q<sub>t</sub> = adsorption capacity at time t (mg/g).

According to Wang et al. (2007), the rate-limiting step in the Pseudo Second Order Equation is the surface adsorption, which is a form of chemisorption. In this process, the two phases interact physiochemically to remove the substance from a solution. As demonstrated in Equation 4 (Darius 2013), the model is typically depicted in a linearized form. Types of Linearized form; plot equation

$$1. \quad t/q = 1/k_2 + \frac{1}{q_e} t ; \quad \frac{1}{q} \text{ vs } t \quad (4)$$

Where  $k_2$  = adsorption rate constant g/mg min. the value of  $q_e$  and  $k_2$  can be obtained from the slope and intercept of the plot of  $1/q_t$  Vs.  $t$  respectively. (Das et al., 2011).

$q_e$  = amount of metal adsorbed at equilibrium.

#### Intraparticle Diffusion Study

In order to study the adsorption mechanism, the intraparticle diffusion-based approach was examined. The following equation is put out to explain the relationship between the amount of sorbent taken up by an adsorbent and the square root of the contact time  $t^{1/2}$  (Chen et al., 2010).

$$q_t = Kid\sqrt{t} + C \quad (5)$$

Where  $q_t$  = amount of adsorbate adsorbed per unit mass of adsorbent. (Unit mg/g),  $t$  = time

$Kid$  = Intraparticle diffusion rate constant (mg/g.min<sup>-1/2</sup>).

The rate constant  $Kid$  of stage 1 is obtained from the slope of the straight line of  $q_t$  Vs  $t^{1/2}$ . (Cui et al., 2019)

### Desorption Kinetic Models Used in this Study

#### First Order Reaction:

A first order reaction depends on the concentration of one reactant and the rate law is

$$Rate = - \frac{d[A]}{dt} = K[A] = K[A] \quad (6)$$

Rearranging and integrating

$$\ln q = - kt + \ln a \quad (7)$$

Where  $q$  = quantity of metal desorbed (mg/kg).  $t$  = time (hr),  $K$  = desorption constant (h<sup>-1</sup>)

#### Second Order Reaction

This is a type of reaction where the sum of the exponents in the corresponding rate law is equal to 2. Such as

$$r = k_2[A]^2 \text{ or } r = k_2[A][B] \quad (8)$$

Where  $k_2$  = rate constant.  $[A]$  = concentration of A,  $[B]$  = Concentration of B

The parabolic diffusion is related to the intraparticle diffusion of equation 2.11.

$$q_t = a + Rt^{1/2} \quad (9)$$

Where  $R$  = desorption rate constant;  $a$  = constant

#### The Power Function

The power function model is also used to test the fit of desorption data. It is given by

$$\ln q_c = ab \ln t \quad (10)$$

Where  $a$  is a constant which indicates the number of surface sites available for desorption.

$b$  is the desorption rate constant it is also a measure of the affinity of the metal to the sites. Increased affinity is indicated by  $1/b$  (Motaghin and Hosseipur 2013).

#### Simple Elovich Kinetic Equation

The Elovich model was developed on the basis of diffusion or chemisorption (Shuang et al., 2018).

The equation is given by

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (11)$$

Where  $\alpha$  = Initial adsorption rate (mg/kg. min),  $\beta$  = Desorption rate constant (kg/mg),  $q_i$  = quantity adsorbed (mg/kg),  $t$  = time.

Linearizing equation (2.28) gives.

$$q_t = \frac{1}{\beta} \alpha t + a \quad (12)$$

Where  $\beta$  = slope = desorption rate constant and  $a$  = intercept which represent the capacity factor. Wahba et al., (2016).

## 2.0 Materials and Methods

### Determination of selected properties of the bone samples

As detailed by Rajwar and Pandey (2014), the EDTA titration method was used to determine the bone calcium content. Using the molybdenum blue method as detailed by Hughes et al., 2019, the phosphate was measured. According to the International Organization for Standardization's description, the total heavy metal contents were found using the aqua regia extraction method (ISO 11466 1985). The fixed carbon was measured using the ASTM3172; ISO1350 technique.

### Determination of the physicochemical properties of the soil

The water's pH was determined using the procedure outlined in ASTM D1293-95 (2013), and the electrical conductivity was measured using a thermometer and an EC meter (Orion Star A212). Scientific Research Firm Fisher

In order to measure soil organic carbon, researchers followed the procedure laid out by Walkley and Black (1947) for wet oxidation. According to the procedure described by Kalir and Madsen (1995), the cation exchange capacity (CEC) was determined. We used the Cotter-Howells and Capron method (1996) to measure the phosphate concentration of the soil. We used the Micro Kjeldahl method, which was described by A.O.A.C. (1990), to determine the percentage of nitrogen. Jenway PFP7 Flame Photometer readings were taken in accordance with ISO 11047:1998 standards to determine the soil potassium concentration. The soil sample's iron oxide concentration was determined according to the procedures described by Khan and Cornfield (1968). Determining the moisture content was done using the A.O.A.C. method (1990).

### Sorption and Desorption Experiment Sorption

#### 2.1 Sorption Experiment

Choko (2017), Aishat et al. (2017), and Ping et al. (2016) outlined the steps to take when conducting the absorption kinetic. Time intervals of 1, 2, 3, 4, 5, 6, 8, 24, 72, 168, 336, 504, and 672 hours were used to repeat the experiment. We used the connection to determine the amount of sorbed.

$$q = (C_0 - C_t) / W * V \quad (13)$$

Where	V	=	Volume of the electrolyte (ml)
	C <sub>0</sub>	=	Initial metal concentration (mg/L).
	C <sub>t</sub>	=	Concentration of the metal at time (hrs.)
	W <sub>1</sub>	=	Weight of soil plus amendment (g)

#### 2.2 Desorption Experiment

Research on the heavy metal desorption by soil amendments was conducted in accordance with the methodology outlined by Ping et al. (2016), Aishat et al. (2017), and Choko (2017). Contact times of 2, 4, 6, 8, 24, 72, 168, 504, 672, and 1344 hours were used to repeat the desorption process. You can find out how much metal is desorbed via

$$q_{des} = \frac{C_1 \times V}{w_1} \quad (14)$$

$$\% \text{ Desorbed} = \frac{q_{desorbed}}{Q_{e \text{ absorb}}} \times \frac{100}{1} \quad (15)$$

Where C<sub>1</sub> = final conc. in mg/L, V = Vol. of the dissolved liquid (ml), W<sub>1</sub> = Weight of the soil mixture (g),  $q_{des}$  = quality desorbed

## Results and Discussions

### Chemical Properties of the Bone Samples.

Selected properties of the animal bones used for the immobilization study are shown in table 1.

**Table 1: 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 <sub>2</sub> O <sub>5</sub> )	%	42.406	38.857	40.488
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 as CaO	%	39.09	32.32	33.27

The bone samples' total carbon (TC) levels vary from 16.76% to 20.92%, with pig bone having the highest TC level. Surface carbon affects sorption, phosphate ion hydro-apatite arrangement, and cadmium ion attraction sites (Abdulrahman et al., 2015). The three bone samples were all excellent immobilization agents, as shown by their high Total carbon levels (Table 1). The bone samples show elevated calcium and phosphate percentages; the pig bone has the greatest concentration, the horse bone the lowest, and the cow bone the highest. According to the results of the bone sample analysis, it belongs to the same family as hydroxyapatite (Ca<sub>5</sub> (PO<sub>4</sub>)<sub>3</sub> OH (HA)), the most prominent member of a vast class of substituted compounds with a comparable structure (Nzihon and Sharrock, 2019).

Solubility, ion exchange, and precipitation make up the fundamental process. Source: Ma et al., 1993. The presence of soluble metals and phosphorus is necessary for the creation of pyromorphite, an insoluble compound. This is according to Joonki (2005). The immobilization sequence for all metals is CBA>PBA>HBA because phosphate and calcium levels in cow bone are higher than in pig and horse bone.

## 2 Physicochemical Properties of the Soil

Some selected physicochemical properties of the soil are presented in Table 2.

**Table 2: Physicochemical properties of the soils.**

Parameter	Units	Clay
Sand	%	32.20
Silt	%	5.60
Clay	%	60.20
Textual	Class	Clay
Ph		6.45
Organic Matter	%	31.736
EC	Ds/m	1228.40
CEC	Cmol/kg	6.22
P <sub>2</sub> o <sub>5</sub>	Cmol/kg	1.12
TN	Cmol/kg	1.63
Tis	Cmol/kg	9.68
Moisture	%	42.30
Cd	mg/kg	0.02
Cr	mg/kg	0.01
Pb	mg/kg	0.30
Fe <sub>2</sub> O <sub>3</sub>	Cmol/kg	0.65
Al <sub>2</sub> O <sub>3</sub>	Cmol/kg	0.21

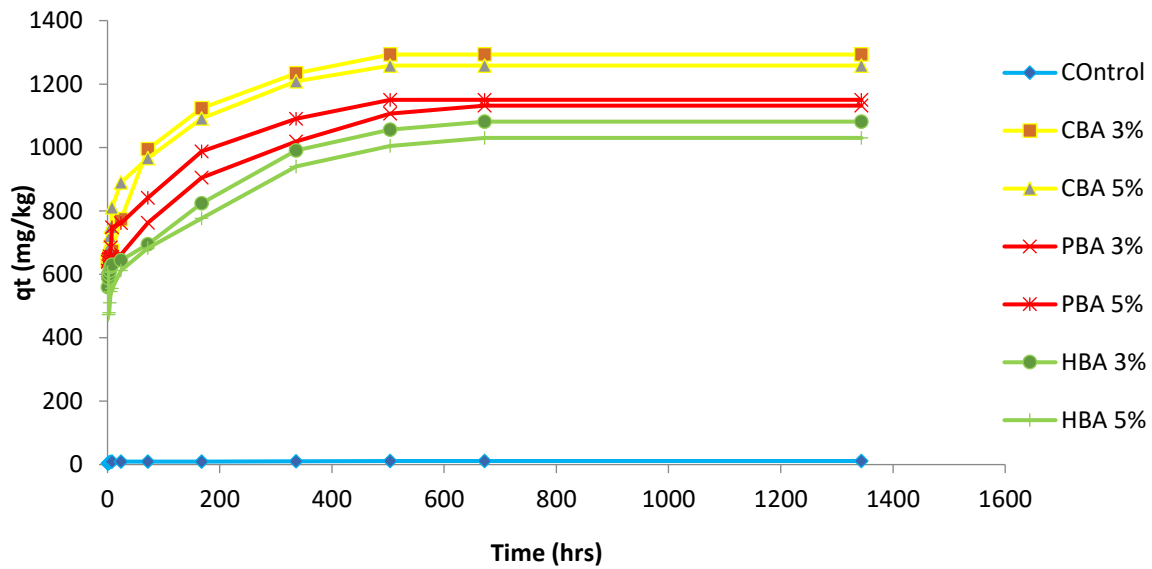
Metal mobility in soils is significantly impacted by the soil texture. Soil clay and mineral oxide particle size distribution is reflected in texture. The adsorption media constituted by these chemicals is significant (Sherene, 2010).

At 6.45, the earth has a pH. Because of their acidity, the soil samples were ideal for desorption and mobility.

There is a significant amount of organic matter in the clay soil that was investigated. According to Sherene (2010), organic matter plays a crucial role in metal sorption and desorption. Because organic matter reduces mobility and bioavailability, it is essential for metal retention in soil. Soil organic matter helps heavy metals stay in the ground, but too much of it might cause complexation reactions that make the metals more soluble (Sherene, 2010).

Low phosphate soils are those with a phosphate level of less than 1.12 Cmol/kg. Sulfate and other anions can often coordinate metal ions to create complexes that are insoluble in water. The immobilization of lead from 39% to 100% was demonstrated by Ma et al. (1995) to be mainly accomplished by phosphate rock, namely flu apatite (Ca10- (PO4)6 Fe). According to He et al. (2015), the soils had a very low lead (Pb) level when compared to the regulatory criteria of 200 mg/kg.

**Sorption Kinetic Studies** The sorption characteristics of the amendments and the soils were studied in order to ascertain how heavy metal cation (Pb) are adsorbed into the soil and amendment matrix. These studies are presented in Fig 1



**Fig 1: Kinetics of Lead Adsorption in Clay Soil**

At 3% and 5% amendment concentrations, the quantity of Pb absorbed by the amendments is shown in Fig. 1. With different amounts of contact time, the metal was adsorbed in mg/kg from a Pb solution with a concentration of 8000 mg/L. From the first hour to the first 72 hours, there was a dramatic rise in sorption (a quick sorption reaction), and then the sorption process sloped downward (slow sorption steps). The findings of other studies (Chokor, 2017; Straw and Spark, 2000) are consistent with this two-stage time-dependent sorption pattern. Overall, the amount of Pb (II) absorbed by the amendment is greater at 5% than at 3%.

**Table 3: Summary table for the pseudo first order sorption of Pb.**

Model parameters	Control	3% CBA	5% CBA	3% PBA	5% PBA	3% HBA	5% HBA
Q mg/kg	0.9925	0.9925	0.99203	0.997902	0.9949	0.99143	0.99243
K <sub>1</sub> /hr <sup>-1</sup>	0.0075	0.0028	0.0080	0.0021	0.0051	0.0086	0.0076
R <sup>2</sup>	0.779	0.9316	0.514	0.8665	0.982	0.7713	0.7867

Table 3 shows the sorption of lead both with and without various additives. The maximum quantity sorbed was low, and the pseudo-first order rate constant k<sub>1</sub> was extremely low as well (0.001-0.0087hr<sup>-1</sup>). According to Mohammed and Mohammed (2010), in order for the sorption process to adhere to the kinetic model, high values of the rate constant and q<sub>m</sub> are required. Sorption data for Pb via CBA, PBA, and HBA did not conform to the pseudo first order kinetic model due to extremely low Q, k<sub>1</sub>, and R<sup>2</sup>, in accordance with this hypothesis. Cheng and Hseu (2002), Kumar and Bandyopadhyay (2006), and Nwabunne and Igbokwe (2008) are among the works that adhered to this tendency.

**Table 4: Summary table for the pseudo second order sorption of Pb.**

Model parameters	Control	3% CBA	5% CBA	3% PBA	5% PBA	3% HBA	5% HBA
Q mg/kg	11.2668	1125.30	1130.40	1111.23	1116.33	1107.30	1000.30
K <sub>2</sub> /hr <sup>-1</sup>	0.1591	0.0410	0.0389	0.0506	0.0425	0.0534	0.0553
R <sup>2</sup>	0.9993	0.9995	0.9996	0.99985	0.9994	0.9981	0.9982

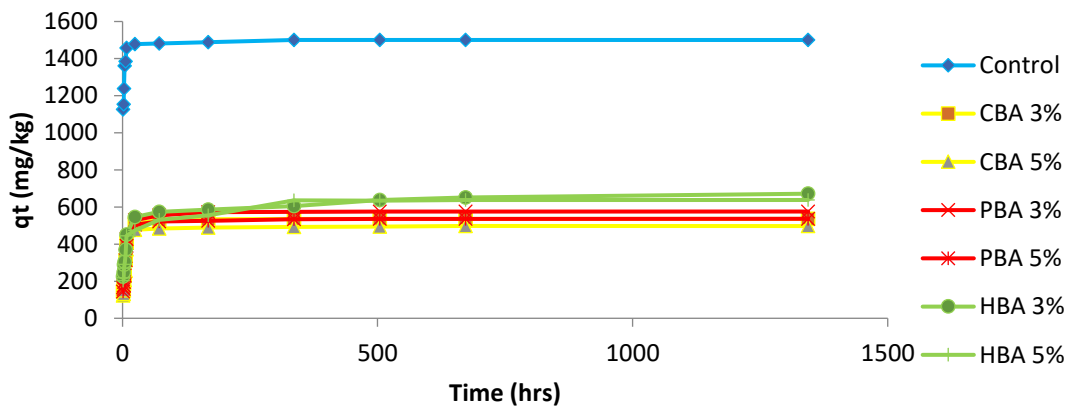
Table 4 displays the outcomes of testing the sorption process using the pseudo-second order kinetic model. High values of K<sub>2</sub>, Q, and R<sup>2</sup> indicate that the pseudo second order model is applicable to the sorption of Pb in clay soil by the CBA, PBA, and HBA to a satisfactory degree.

**. Desorption Kinetic Studies**

A graph of qt<sub>des</sub> against time was used to study the desorption mechanism of heavy metals in the soil (Fig. 2). Two different rates of 3% and 5% were used to apply the changes. Using CBA, PBA, and HBA reduced the amounts of metal desorbed or released from 1500.05 mg/kg to 488 mg/kg, 525 mg/kg, and 595 mg/kg, respectively, as shown in the figure. The study conducted by Saffari et al. (2015) on the stability of nickel in carcinogenic soils with inexpensive amendments also reached a similar conclusion. To find the most accurate model, we utilized the rate constants (k<sub>1</sub>), correlation coefficient (R<sup>2</sup>), and standard error (SE). The selection of the best-fitting model was based on comparatively high values of (R<sup>2</sup>) and low values of (SE). Here is how the standard error was determined:

$$SE = \left[ \frac{\sum(E - E^1)^2}{n-2} \right]^{0.5} \tag{16}$$

Where E and E<sup>1</sup> are the experimented and predicted or calculated amounts of metal released in soil at time it, respectively and n are the number of measurements



**Fig 2: Kinetics of Pb Desorption in Clay Soil.**

As shown in table 5, the first-order kinetic model summarizes desorption. According to what is shown, desorption of lead (Pb) in clay soil by CBA, PBA, and HBA did not conform to the first-order kinetic model due to low R<sup>2</sup> and k<sub>1</sub> and large SE..

**Table 5: Summary Table for the first order desorption of Pb Parabolic Diffusion Model**

Model Parameters	Control mg/kg	3% CBA mg/kg	5% CBA mg/kg	3% PBA mg/kg	5% PBA mg/kg	3% HBA mg/kg	5% HBA mg/kg
Q <sub>des</sub>	1700.44	496.32	393.70	595.95	520.13	753.0	634.17
K <sub>1</sub>	0.000123	0.000667	0.00072	0.000663	0.000685	0.000616	0.000665
R <sup>2</sup>	0.2181	0.2593	0.266	0.277	0.271	0.382	0.387
S.E	206.212	198.526	200.343	196.341	197.464	175.532	175.532

Data analysis for lead desorption into soil matrix by CBA, PBA, and HBA showed this model graphing qt against t<sup>1/2</sup>. Table 6 displayed the constant K<sub>p</sub>, R<sup>2</sup>, and SE. K<sub>p</sub> is the constant that represents the amount desorbed, and qt is the intraparticle or parabolic diffusion rate. It is evident from table 6 that the amendments in the soil desorbed Pb in the following order: CBA < PBA < HBA. It is possible that CBA's higher phosphate and calcium concentration explains why it desorbs metals from soil at a slower rate than HBA and PBA. Compared to PBA and HBA, CBA forms a more insoluble pyromorphite. Metal mobility in soil is hindered by the insoluble pyromorphite. Soil phosphate availability directly correlates to immobilization. This

explains why the 3% of changes had less of an immobilization effect than the 5%. There is a lack of R<sup>2</sup> and SE. It can be inferred from the kinetic data that the parabolic diffusion model is not applicable, as indicated by the R<sup>2</sup> < 0.7 and SE > 26.0. In 2015, Saffari et al. also found something similar.

**Table 6: Summary Table for Parabolic Diffusion Kinetic model for the desorption of Pb**

Model	Control	3%	5%	3%	5%	3%	5%
Parameters	mg/kg	CBA	CBA	PBA	PBA	HBA	HBA
Q	136.179	286.394	251.633	304.791	280.277	345.702	318.625
K <sub>p</sub>	7.495	10.154	9.9126	10.9516	10.3572	11.8182	12.2503
R <sup>2</sup>	0.3963	0.5091	0.5188	0.5394	0.5257	0.6838	0.7075
S. E	88.45	46.231	42.116	45.232	44.366	33.45	24.65

#### Power Function Model

A graph showing the relationship between qt and ln t was used to illustrate this model in the context of lead desorption data into soil matrix as a result of CBA, PBA, and HBA amendments. The model was described using the constants a, b, R<sup>2</sup>, and SE, which are displayed in Table 7. The amount of heavy metals desorbed is represented by the constant 'a,' while the specific desorption rate at unit time is represented by the constant 'b' (Venekatah et al., 2010). Since the correlation coefficient R<sup>2</sup> is less than 0.90, the data does not fit the power function model, as shown in Table 7.

**Table 7: Summary Table for the Power Function kinetic model for the desorption of Pb**

Model	Control	3%	5%	3%	5%	3%	5%
Parameters	Mg/kg	CBA	CBA	PBA	PBA	HBA	HBA
A	1193.64	150.838	130.972	173.481	154.583	233.329	209.045
B	0.0345	0.1833	0.1988	0.0789	0.1852	0.1494	0.1615
R <sup>2</sup>	0.6746	0.7689	0.7721	0.7888	0.7797	0.8780	0.8915
S. E	74.321	68.32	68.536	0.654	0.672	0.457	0.1451
A	1324.425	437.935	373.565	489.954	439.550	660.455	557.526

#### Elovich Kinetic Model

Plotting qt against ln t for the examination of data for desorption of Pb, Cr, and Cd into the soil matrix by CBA, PBA, and HBA provided evidence of this model. You may find the model's analysis constants  $\alpha$ ,  $\beta$ , R<sup>2</sup>, and SE in table 8. The basic premise of the Elovich equation is that chemisorption activation energies vary throughout the heterogeneous sorbent active surfaces (Mehranz, 2015). Desorption rate constant  $\beta$  increased from 0.0124 to 0.1472 (mg/kg)<sup>-1</sup> and initial lead decreased from 1250.63 (mg/kg) to 736.422 (mg/kg) as a result of the CBA adjustment. When other amendments such as PBA and HBA were applied, the value of  $\alpha$  decreased relative to the control and  $\beta$  increased, resulting in a similar impact.

**Table 8: Summary Table for the Simple Elovich Kinetic Desorption of Pb**

Model	Control	3%	5%	3%	5%	3%	5%
Parameter	mg/kg	CBA	CBA	PBA	PBA	HBA	HBA
$\alpha$	1250.631	855.362	736.4223	923.413	878.3764	965.211	920.320
$\beta$	0.01245	0.01352	0.01472	0.01304	0.01340	0.01860	0.01933
R <sup>2</sup>	0.7087	0.8406	0.83999	0.86313	0.8540	0.9280	0.850
S. E	61.426	16.274	16.525	16.272	11.255	11.266	13.425

#### Conclusion

There are trace amounts of heavy metals in all of the soil samples assessed. This study's comparative data analysis shown that Horse Bone Ash (HBA), Pig Bone Ash (PBA), and Cow Bone Ash (CBA) can immobilize and remediate Clay soil. Contrasted with the soil's efficiency, which is ranked from laterite to clay to sandy, the immobilizing agent's efficiency is in the order of CBA>PBA>HBA. Studies on the sorption of lead onto CBA, PBA, and HBA followed a pseudo second-order kinetic model rather than a first-order second-order parabolic diffusion or power function fit, and studies on the desorption of lead followed an Elovich kinetic model.

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