# KINETICS OF CHROMIUM IMMOBILIZATION IN SOILS USING ANIMAL BONES

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**Abstract -** The kinetics of chromium immobilization from contaminated clay, sandy, and lateritic soil using cow bone ash (CBA), pig bone ash (PBA), and Horse bone ash (HBA) were studied. The experimental study concentrated on the adsorption and desorption of the chromium heavy metal. The analysis of the bone samples reveals that they contain a high percentage of calcium phosphate with increasing order of CBA > PBA > HBA while the metal immobilization in the soils is in the order Laterite soil > Clay soil > sandy soil. The experimental results were fitted into pseudo-first order and second order kinetic models and the results showed a good fit of the adsorption process into pseudo second order model as $R^2$ are all above 0.999 and the standard errors are low, while the desorption process did not fit into any of the kinetic models. It is therefore recommended that the results be tried in other kinetic models.
**Keywords: chromium, immobilization, animal bones, laterite soil, sandy soil**

## 1.1    Introduction
**Review of related literature**
Chromium is a cubic, body-centered crystal structure that does not occur naturally but in oxide form. The oxide of the metal is acidic. Its color is silver grey, and it can be highly polished (Amanda et al., 2013: Wuana and Okiemen 2011; Leghlimi et al., 2015).

It occurs in almost all oxidation states ranging from 2 to 6 but is mostly stable in trivalent and hexavalent forms. Chromium (Cr) is one of the non-essential metals produced by big industries like oil and coal, textiles, tanneries, electroplating, and metallurgical which cause health issues in humans and animals as well as marine life. (Kumpiene et al., 2015).

Chromium compounds find extensive applications across various industries including electroplating, metal finishing, production of magnetic tapes, pigment manufacturing, leather tanning, wood preservation, chemical production, and brass manufacturing, as well as in the electrical and electronic equipment industry (Safari et al., 2014).

In spite of the importance of chromium in industries, it causes various disease and disorders like, cancer, hypertension, chronic kidney disease, brain and liver damage, anemia if in excess. It also has adverse effect on plant growth and soil micro-flora (Shaheen et al., 2008; Mohan et al., 2006; Mohan and Pittman 2007). Chromium and its compounds can be absorbed by humans through ingestion, dermal contact and inhalation.

At low soil pH, chromium III is the dominate form hence, more stable, less mobile and toxic than chromium VI. The mobility of chromium is influenced by the sorption characteristics of the soil, including clay content, iron oxide content, and the quantity of organic matter present. Soluble chromium complexes that remain unabsorbed can migrate from the soil into groundwater. Elevated pH levels enhance the mobility of Cr (VI) and consequently increase its leaching potential. (Wuana and Okieimen, 2011).

Remediation by immobilization technology is the alteration of the original soil metal concentration through sorption, desorption, precipitation and complexion processes by the use of organic and inorganic material so as to accelerate the attenuation of metal mobility and toxicity in the soils. The movement of heavy metals within soil heavily relies on its characteristics, particularly its organic matter content, grain size distribution, and soil pH.

Generally, heavy metals exhibit greater solubility and mobility in acidic environments. Consequently, acidic soils typically facilitate the dispersion of contaminants, whereas alkaline soils tend to accumulate heavy metals. (Wuana and Okieimen 2011; Khan et al., 2008).

Immobilization kinetics involves assessing the adsorption/desorption rate, modeling the process, and predicting information regarding the interaction between adsorbent and adsorbate (Amanda et al., 2013). In this study, two distinct models were employed: the Pseudo-first-order and pseudo-second-order models (Hashema and El-khiraig, 2013; Priyantha and Bandaranayaka, 2011).

**Pseudo-First-Order Equation**
The pseudo-first-order rate equation for liquid solid adsorption system is expressed as follows:

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

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$^{-1}$) is the rate constant of pseudo-first order reaction. The linearized equation is $x = X\,(1 - e^{-kt})$ (2)

Equation (2) is popularly used as

$$log(q_m - q_t) = \log(q_m) = \frac{-K}{2.303}t \quad (3)$$

$$or \ln(q_m - q_t) = \ln q_m - Kt \qquad (4)$$

Where $q_m$ = adsorption capacity at equilibrium mg/g

$q_t$ = adsorption capacity at time t (mg/g).

**Pseudo Second Order Equation**
In this model, the surface adsorption process is identified as the rate-limiting step, characterized by chemisorption, wherein the removal from a solution occurs due to physiochemical interactions between the two phases (Wang et al., 2007). Typically, the model is presented in a linearized form, represented by Equation 5 known as the pseudo-second-order kinetic equation (Dariush, 2013).

$$q = q_t - \left(\frac{1}{k2q_t}\right)\frac{q}{t} \ ; \ q \ vrs \ {}^{q}/_{t} \qquad (5)$$

Where $k_2$ = adsorption rate constant g/mg min (Das et al., 2011).

**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

$$q_t = ae^{-kt} \qquad (6)$$

Where $q_t$ = qty. g metal desorbed mg/kg. t = time (hr.). K = desorption constant (h$^{-1}$)

**Second Order Reaction**
This is a type of reaction where the power of the exponents in the corresponding rate law is equal to 2. Such as

$$r = k_2[A]^2 \ or \ r = k_2[A][B] \qquad (7)$$

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

Eigbike and Salihu (2023) conducted a study on the efficacy of Calcium Phosphate Amendment and Phosphate-solubilizing Fungi (Penicillium sp) in immobilizing heavy metals in contaminated soils. The results demonstrated a significant reduction in the concentrations of several heavy metals, including Zn, Cr, Cd, Pb, Fe, and Ni, within a two-week period Chokor (2017) studied immobilization of heavy metals in sandy- loam soil of Sapele metropolis by adsorption- desorption and discovered metal adsorption increases with concentration and the distribution coefficient ($K_d$) increases with decrease concentration of the soil solution. Khan et al. (2012) investigated the impact of amendments on the chemical immobilization of heavy metals in soils contaminated by sugar mills. The findings revealed that DTPA extractable metals exhibited a gradual increase over time, with maximum values observed after 90 days of incubation. It was concluded that farmyard manure (FYM) and diammonium phosphate (DAP) are viable options for mitigating the risk of heavy metal contamination in polluted soil.

Che and Rosazlin (2014) reviewed in- situ immobilization of selected Heavy Metals in soils using agricultural wastes and industrial by-products. They concluded that there were great potentials in the use of bio char and

industrial byproducts for heavy metal immobilization in contaminated soils.

However, there are currently limited studies on the kinetics of heavy metal immobilization in contaminated soils using animal bones. This research focused on the kinetics of chromium immobilization using Cow bone Ash (CBA), Horse Bone Ash (HBA) and Pig Bone Ash (PBA)

## 2.1 Materials and Method
### Materials

Cow bone, Horse bone, Pig bone, Clay soil, Sandy soil, and Lateritic soil. Other materials used include: distilled water, sodium hydroxide (NaOH), Hydrochloric acid, Lead nitrate (PbNO$_3$), Cadmium chloride (CdCl$_2$.H$_2$O), Chromium Nitrate (CrNO$_3$), Magnesium chloride (MgCl$_2$), sodium ethanoate (CH$_2$COON$_a$), DTPA- Diethylene-tri-amine pent acetic acid, Triethanolamine (TEA), Potassium Dichromate (K$_2$Cr$_2$07), Ferrous Ammonium sulphate (Fe(NH$_4$)$_2$ (Sp): 6H$_2$O phosphoric acid (H$_3$P0$_4$), Sodium fluoride (NaF), Diphenyl amine (C$_6$H$_5$NH$_6$H$_5$

Atomic Absorption photo spectrophotometer (AAS), Model; AA 430 N, pH meter, Laboratory drying Oven, Magnetic Stirrer, Electromagnetic sieve shaker, Electric weighing balance Electric Furnace (CWF 12/5No. 402104), Hot plate; Centrifuge, Agitator, Measuring Cylinders

## 2.2 Method
### 2.2.1 Samples Collection and Preparation

Three different types of soil (0-20cm) dept. were collected from three different locations in Enugu State, Nigeria. The Clay soil was collected from Amagunze. Lat. 6.382541 and long. 7.486532 in Nkanu East Local Government Area of Enugu State, Nigeria. Lateritic soil was collected from Emene. Lat. 6.488203 and long. 7.57282 in Enugu East local Government Area of Enugu State

Sandy Soil was collected from Obollo-Afor Lat 6.920592475 and Long 752099387 in Udenu Local Government Area of Enugu State

**Collection of the Bone Samples (amendments).**

The three immobilizing agents were collected as follows

(1) Cow Bone was collected at Oye, Emene Central Abattoir in Enugu East L.G.A.
(2) Pig Bone was also collected at Oye, Emene Central Abattoir
(3) Horse Bone was collected at the Abattoir of the Obollo -Afor main market in Udenu L.G.A. of Enugu State.

### 2.2.2. Preparation of the Amendments.

The bone samples were prepared according to the method described by (AbdulRahman et al., (2016). The bones underwent multiple washes with water, were then cut into pieces using a cutlass, and subjected to repeat rinsing to eliminate surface impurities. Following this, the bones were washed with de-ionized water and placed in an oven set at 80°C for drying. Once dried, they were crushed using a motorized crusher and subsequently transferred to a furnace, where they were heated at 700°C for a duration of five (5) hours. The phosphate content of the bone was analyzed using the Cotter-Howells and Capron method (1996).

### 2.2.3. Chemical Analysis of the Soil Samples

The pH was determined using British standard ISO 10390. Organic matter content, was determined using Walkley and Black's method (1947) Electrical Conductivity (EC) was determined using EC meter, CEC, Total Nitrogen and particle size distribution of the contaminated soil sample were determined according to the procedure described by Kalir and Madsen (1995), modified kjeldahl method ISO 1126 and the hydrometer method respectively. Heavy metal analysis of the contaminated soil sample and bone. The total soil & bone heavy metal contents were determined by the method of aqua regia extraction as described by the International Organization for Standardization (ISO 11466 1995). The analysis was performed with an Atomic Absorption photo spectrometer (AAS) model AA340N.

### 2.2.4. Spiking of the Soil with the Heavy Metal

The soils were spiked following the method described by Noha et al., (2013). 1kg of soil and 3g of amendment were ground in a wood plate and grinding rod. The material was sieved with 2mm sieve. The mass of the metal specie CrCl$_3$.

6H20 was added. The whole mass was placed in a polyethylene bag and shaken thoroughly. The experiment was repeated with 5g of the amendments.

### 2.2.5. Kinetic Experiment

**Sorption and Desorption Experiment Sorption**

**Sorption Experiment**

The absorption kinetic was done according to the procedure described by Aishat, et al., 2017 and Choko, (2017). 3g and 5g of the incubated samples were each weighed into a 500 ml flask. 25ml of DTPA-TEA solution of conc. 0.001 mol $L^{-1}$ was added. The mixture was agitated and equilibrated at room temperature $27^{o}C$ for 1 hr. The solution was separated by filtration using what man 42 filter paper. The heavy metals cation concentration in each filtrate was determined by Atomic Absorption spectrophotometer (AAS) model AA340 N. The change in the initial and final concentration after the reaction period were assumed to be adsorbed by the amendments. The experiment was repeated at time intervals 1, 2, 3, 4, 5, 6, 8, 24, 72, 168, 336, 504, 672 hours. The quantity sobbed was calculated from the relation

$$q = \frac{(co-ct)v}{w} \qquad (8)$$

Where V =Volume of the electrolyte (ml), $C_o$ =Initial metal concentration (mg/L)., $C_t$ = Concentration of the metal at time (hrs.), $W_1$ = Weight of soil plus amendment (g)

### 2.2.6. Desorption Experiment

The desorption of the heavy metals by the amendments from the soils was studied following the method described by Aishat *et al.*, (2017) and Choko (2017). To the residue of the heavy metal enriched soil separated from the supernatant solution during the sorption experiment, 25ml of DTPA-TEA solution of 0.001 mol $L^{-1}$ concentration was added to each. The suspension was shaken for 1hr at room temperature ($27^{o}C$). The supernatant was centrifuged at 800 rpm for 15 minutes and the Cr desorbed into solution was determined by atomic absorption spectrophotometer Model AA 430 N. Desorption process was repeated at contact time of (2, 4, 6, 8, 24, 72, 168, 504, 672 and 1344 hours) The quantity of metal desorbed is given by

$$q_{des} = \frac{C_1 \, x \, V}{w_1} \, (9)$$

Where $C_1$ =final conc. in mg/L, V = Vol. of the dissolved liquid (ml), $w_1$ = Weight of the soil mixture (g). $q_{des} = $ quality desorbed

### 3.0. Data Presentation and Analysis

**Table 1: Selected Chemical Properties of the bone samples**

| Parameter | | | Bone samples | |
|---|---|---|---|---|
| | Units | CBA | HBA | PBA |
| Total carbon (TC) | % | 17.80 | 16.76 | 20.92 |
| Phosphate (P$_2$O5) | % | 42.406 | 33.857 | 40.488 |
| Calcium oxide (CaO) | % | 49.295 | 45.664 | 46.467 |
| Chromium (Cr) | mg/kg | 0.001 | 0.001 | 0.02 |

Total carbon (TC) of the bone sample ranges from 16.76% to 20.92% with pig bone the highest. According to AbdulRahman et al., 2016, carbon influences sorption and the hydro apatite arrangement of the phosphate ion and provides sites for the attraction of metal ions. The high values of the Total carbon in the three bone samples (Table 1) is an indication that they are all effective immobilization agents. The bone samples contain high percentages of phosphate, with the cow bone having the highest concentration followed by the pig bone

and the least is the Horse bone. The bone samples show that it is an appetite family with hydroxyapatite ($Ca_5$ ($PO_4$)$_3$ OH (HA), with the leading member of large class of substituted compounds of similar structure (Nzihon and Sharrock, 2019). Since cow bone has higher phosphate than pig and Horse bone, the immobilization follow the sequence CBA>PBA>HBA for all the metals.

From table 1, it was observed that the values obtained for concentration of Cr ranging from (0.001 -0.002 mg/kg) was within the

permissible limit for WHO/FAO and E.U standards. This is insignificant to the WHO/FAO and E.U. standards of 1.3 mg/kg and 0.3 mg/kg respectively. (Mohamed and Folorunsho, 2015).

**Table 2: Selected physiochemical properties of the soils.**

| parameter | Units | Before spiking with chromium | | | After spiking with chromium | | |
|---|---|---|---|---|---|---|---|
| | | Clay | Sandy | Laterite | Clay | Sandy | Laterite |
| Sand | % | 32.20 | 77.20 | 20.28 | 32.22 | 77.25 | 21.12 |
| Silt | % | 5.60 | 7.42 | 55.36 | 5.64 | 7.48 | 55.65 |
| Clay | % | 60.20 | 15.38 | 24.36 | 60.19 | 15.49 | 24.44 |
| Textural | % | Clay | Loamy Sand | Silt Loam | Clay | Loamy Sand | Silt Loam |
| pH | | 6.45 | 6.82 | 6.54 | 7.44 | 7.86 | 7.77 |
| OM | % | 31.74 | 4.20 | 2.46 | 31.77 | 4.24 | 2.52 |
| EC | Ds/m | 1228.40 | 18.66 | 25.36 | 1228.46 | 18.88 | 25.40 |
| CEC | Cmol/kg | 6.22 | 5.02 | 5.61 | 6.23 | 5.05 | 5.65 |
| P205 | Cmol/kg | 1.12 | 1.45 | 0.98 | 44.13 | 44.65 | 44.46 |
| TN | Cmol/kg | 1.63 | 1.82 | 1.70 | 1.64 | 1.81 | 1.72 |
| Cr | Mg/kg | 0.01 | 0.02 | 0.03 | 5.02 | 5.04 | 5.02 |

The texture of the soil were clay, loamy sand and silt loam. 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 (Sherene, 2010).

The clay soil retained higher number of metals than the sandy soil. This means that the higher the clay mineral content of soil the higher the adsorption capability of that soil.

The pH of the soils ranges from 6.45 to 6.82. Metal sorption increased with increasing pH. That is, the lower the pH value the more metals can be found in solution and thus more metal is mobilized. The pH of the soil samples was all acidic and hence favored desorption or mobility. The mobility of heavy metals in the soil were generally high at low pH (Shastian et al., 1998).

The organic content of the studied clay soil was very high when compared with that of the sandy and lateritic soil as can be seen in Table 4.1. Organic matter is a key parameter for metal sorption and desorption (Sherene, 2010). Organic matter plays a crucial role in the soil's ability to retain metals within its solids, thereby reducing their mobility and bioavailability.

However, while organic matter facilitates the retention of heavy metals in soil, an excess of it can lead to increased metal solubility due to complexation reactions (Sherene, 2010).

The clay soil organic matter is 31.72% which is much higher than sandy soil of 4.20% and Lateritic soil of 2.46% hence, the clay soil would immobilize better than the sandy soil. Organic matter increases the adsorptive surface to which the metal clings. The phosphate content of the three soils ranged from 0.98 – 1.45 (Cmol/kg). They are therefore classified as low phosphate soils. Generally, anions such as sulphate can coordinate metal ions to form insoluble complexes. The content of chromium (Cr) in the soils were very low compared to the regulatory standards of 11.0 mg/kg as stated by He et al., (2015).

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

| Soil | Model parameters | Control | 3% CBA | 5% CBA | 3% PBA PBA | 5% PBA | 3% HBA | 5% HBA |
|------|------------------|---------|--------|--------|-----------|--------|--------|--------|
| Clay | $q_m$/kg | 0999 | 0.9961 | 0.9928 | 0.9939 | 0.9924 | 0.9933 | 0.9949 |
|      | $K_1$/hr$^{-1}$ | 0.0001 | 0.0039 | 0.0072 | 0.0061 | 0.0076 | 0.0067 | 0.0051 |
|      | $R^2$ | 0.31 | 0.785 | 0.7915 | 0.7872 | 0.7777 | 0.7778 | 0.786 |
| Sand | $q_m$/kg | 0.9982 | 0.9976 | 0.9986 | 0.9985 | 0.9987 | 0.9985 | 0.9989 |
|      | $K_1$/hr$^{-1}$ | 0.002 | 0.0024 | 0.0014 | 0.0015 | 0.0013 | 0.0015 | 0.0011 |
|      | $R^2$ | 0.6759 | 0.7409 | 0.7633 | 0.8003 | 0.7234 | 0.7943 | 0.7656 |
| Laterite | $q_m$/kg | 0.9960 | 0.9963 | 1.0331 | .09984 | 0.9988 | 0.9985 | 0.9993 |
|      | $K_1$/hr$^{-1}$ | 0.004 | 0.0037 | 0.0033 | 0.0016 | 0.0012 | 0.0015 | 0.0007 |
|      | $R^2$ | 0.8191 | 0.894 | 0.5517 | 0.6078 | 0.6169 | 0.564 | 0.500 |

The sorption of Cr in Clay, Sandy, and Lateritic Soils without and with different amendments as given in Table 3, can be seen clearly that the pseudo-first order rate constant $k_1$ was very low (001-0087hr$^{-1}$), the maximum quantity sobbed was also low. Mohammed and Mohammed, (2010) pointed out that the values of the rate constant and $q_m$ must be high for the sorption process to follow the kinetic model. Following this theory, a cursory look at Tables 3-4 showed that the $q_m$ and $k_1$ calculated for all the soils were very low. All the $R^2$ values are less than 0.81. Therefore, the data for the sorption of Cr from Clay, Sandy and Lateritic soils by CBA, PBA and HBA did not fit into the pseudo first order kinetic model. Some works that followed this trend include Cheng and Hseu (2002); Nwabunne and Igbokwe (2008).

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

| Soil | Model parameters | Control | 3% CBA | 5% CBA | 3% PBA | 5% PBA | 3% HBA | 5% HBA |
|------|------------------|---------|--------|--------|--------|--------|--------|--------|
| Clay | $q_m$/kg | 11.286 | 111.942 | 119.047 | 107.526 | 112.359 | 105.263 | 104.26 |
|      | $K_2$/hr$^{-1}$ | 0.0866 | 0.04228 | 0.04186 | 0.04388 | 0.04288 | 0.0445 | 0.0431 |
|      | $R^2$ | 0.9993 | 0.9998 | 0.9998 | 0.9999 | 0.9998 | 0.9999 | 0.9999 |
| Sand | $q_m$/kg | 5.5148 | 93.437 | 101.010 | 89.285 | 85.47 | 80.00 | 75.757 |
|      | $K_2$/hr$^{-1}$ | 0.1566 | 0.0466 | 0.0451 | 0.0474 | 0.0482 | 0.0504 | 0.0520 |
|      | $R^2$ | 1 | 1 | 0.999 | 0.999 | 1 | 1 | 1 |
| Laterite | $q_m$/kg | 7.633 | 109.83 | 113.63 | 103.09 | 100 | 93.45 | 90.09 |
|      | $K_2$/hr$^{-1}$ | 0.1054 | 0.0425 | 0.0426 | 0.0896 | 0.0924 | 0.07820 | 0.0727 |
|      | $R^2$ | 0.998 | 0.9998 | 0.9999 | 1 | 0.999 | 1 | 1 |

The analysis of the data for the sorption of Cr in Clay soil, Sandy and Laterite soil by the CBA, PBA and HBA were performed. The values of the rate constant $K_2$, $q_m$ and $R^2$ were calculated and presented in Tables 4. The values of the calculated equilibrium sorption ($q_m$) were high. The correlation coefficient $R^2$ was also very high all greater than 0.99. Therefore, the pseudo second order model is satisfactorily applicable to the sorption of Cr in clay soil by the CBA, PBA and HBA. The applicability of second-order to the sorption data of into CBA, PBA and HBA indicated that the concentration of both the amendment (CBA, PBA & HBA) and the metal ions are involved in the rate determining step and the sorption process can be referred as chemisorption. It was also observed from tables 4 that the sorption of the metals by the amendments from the soil follows the trend of Lateritic Soil > Clay Soil > Sandy Soil. The reason could be that dissolved metals are attached to the surfaces of particulate matter notably, iron, manganese, aluminum oxide minerals, clay, and organic matter. These hydrous oxides form a covalent bond inner-sphere metal surface complexes through which metal sorption occurs. In addition, the metal

hydroxide precipitate phases are formed thus immobilizing and stabilizing the metals in the soil. This is in agreement with the work done by Wuana and Okiemen (2011)

**Table 5: Summary Table for the first-order desorption of Cr**

| Soil | Model | Control | 3% | 5% | 3% | 5% | 3% | 5% |
|------|-------|---------|-----|-----|-----|-----|-----|-----|
|  | Parameters | mg/kg | CBA | CBA | PBA | PBA | HBA | HBA |
|  | Qdes | 642.54 | 253.53 | 233.41 | 273.76 | 252.38 | 295.50 | 284.93 |
|  | $K_1$ | 0.0003039 | 0.001153 | 0.00112 | 0.00109 | 0.001069 | 0.000955 | 0.00099 |
| Clay | $R^2$ | 0.7055 | 0.6149 | 0.4247 | 0.5485 | 0.4649 | 0.5520 | 0.9737 |
|  | S. E | 75.156 | 81.217 | 93.32 | 74.32 | 73.34 | 76.76 | 90.32 |
|  | Qdes | 687.47 | 291.01 | 275.03 | 321.05 | 298.83 | 334.80 | 325.20 |
| Sandy | $K_1$ | 0.000113 | 0.000455 | 0.00047 | 0.00038 | 0.000399 | 0.000364 | 0.00035 |
|  | $R^2$ | 0.5263 | 0.6001 | 0.55941 | 0.5324 | 0.52151 | 0.53672 | 0.5125 |
|  | S. E | 77.42 | 78.261 | 76.33 | 76.33 | 76.43 | 77.32 | 75 |
|  | Qdes | 546.47 | 162.30 | 150.83 | 190.50 | 176.03 | 222.68 | 208.06 |
| Lateritic | $K_1$ | 0.000199 | 0.000769 | 0.00077 | 0.00069 | 0.000723 | 0.000701 | 0.694 |
|  | $R^2$ | 0.2989 | 0.30299 | 0.28463 | 0.33175 | 0.300194 | 0.38503 | 0.3505 |
|  | S. E | 183.40 | 177.33 | 180.45 | 165.76 | 167.50 | 170.42 | 72 |

The first-order kinetic model for desorption of Chromium by bio-sorbent materials from clay soil, sandy soil and Lateritic soils are shown in Table 5. The coefficients of determination $R^2$ is less than 0.6 and the standard errors are higher than 70 in all the soils. It can therefore be concluded that desorption of Cr in clay soil, sandy soil and lateritic soil by CBA, PBA and HBA did not fit into the first order kinetic model. The reason could be attributed to the heterogeneous nature of the desorbing surfaces. First order reactions are attributed by weak bonding like that of Vander wall's type which are always associated with homogenous desorbing surfaces. Similar result was obtained by Saffari et al., 2014. The rate constants ($K_1$), correlation coefficient ($R^2$) and standard error (SE) were used to determine the best fitted model. The selection of the best-fitted model was based on relatively high values of the coefficient of determination (R2) and low values of standard error estimates (SE). The standard error was computed using the following formula:

$$SE = \left[\frac{\sum(E - E1)^2}{n-2}\right]^{0.5} \qquad (10)$$

Where E and E1 represent the experimented and predicted (or calculated) amounts of metal released in soil at time t, respectively, and n is the number of measurements

**Table 6: Summary Table for the Second order desorption of Cr**

| Soil | Model | Control | 3% | 5% | 3% | 5% | 3% | 5% |
|------|-------|---------|-----|-----|-----|-----|-----|-----|
|  | Parameter | Mg/kg | CBA | CBA | PBA | PBA | HBA | HBA |
|  | Qdes | 482.085 | 111.811 | 101.127 | 119.69 | 108.183 | 159.539 | 159.539 |
|  | $K_2$ | $3.27 \times 10^{-7}$ | $5.00 \times 10^{-6}$ | $6.155 \times 10^{-6}$ | $4.614 \times 10^{-6}$ | $5.45 \times 10^{-6}$ | $3.15 \times 10^{-6}$ | $3.15 \times 10^{-6}$ |
| Clay | $R^2$ | 0.3988 | 0.3088 | 0.3843 | 0.3805 | 0.3015 | 0.389 | 0.389 |
|  | S. E | 121.432 | 140.261 | 120.360 | 121.763 | 142.560 | 121.721 | 120.812 |
|  | Qdes | 555.866 | 249.904 | 218.263 | 246.620 | 290.796 | 282.094 | 282.094 |
| Sandy | $K_2$ | $1.966 \times 10^{-7}$ | $3.29 \times 10^{-7}$ | $1.82 \times 10^{-6}$ | $1.41 \times 10^{-6}$ | $1.01 \times 10^{-6}$ | $1.25 \times 10^{-6}$ | $1.12 \times 10^{-6}$ |
|  | $R^2$ | 0.505 | 0.40191 | 0.4712 | 0.4361 | 0.4744 | 0.474 | 0.4429 |
|  | S. E | 98.723 | 96.221 | 96.556 | 95.471 | 96.342 | 96.201 | 95.555 |
|  | Qdes | 398.40 | 72.164 | 64.229 | 90.809 | 79.625 | 102.29 | 94.629 |
| Lateritic | $K_2$ | $5.207 \times 10^{-7}$ | $9.73 \times 10^{-6}$ | $1.11 \times 10^{-5}$ | $7.07 \times 10^{-6}$ | $8.42 \times 10^{-6}$ | $6.04 \times 10^{-6}$ | $5.57 \times 10^{-6}$ |
|  | $R^2$ | 0.2589 | 0.219 | 0.2015 | 0.236 | 0.215 | 0.282 | 0.251 |
|  | S. E | 167.521 | 170.231 | 171.521 | 167.23 | 171.525 | 166.516 | 166.626 |

Table 6 shows the second order kinetic desorption of the metal from the soils by the amendments. The coefficient of determination ($R^2$) is than 0.5 and standard error (SE) is above 95.0 were obtained for the metal desorption in Clay, Sandy and Lateritic soils by the bone

samples. Non fitting of chromium desorption kinetic into second order model was also observed by Labornowski et al., (2008). The reason for non-fitting into the second order kinetic model may be that desorption mechanism cannot be described by a simple rate equation because desorption of metals in soils are affected by many mechanisms such as adsorption, desorption, complexation, precipitation, and ion exchange (Saffari et al., 2014).

## Conclusion and Recommendations

In conclusion, cow bone ash (CBA), pig bone ash (PBA) and horse bone ash (HBA) are good sorbents for chromium immobilization in contaminated soil. The chemical analysis reveals that they contain phosphates in the order of CBA>PBA>HBA while the soil is in the order of lateritic>Clay>Sandy in respect to the extent of chromium immobilization. The key immobilization processes considered are adsorption and desorption. The adsorption process is well fitted into the pseudo second order kinetic model for all the bones and soils while the desorption process neither fits into the first order nor the second order. It is recommended that desorption process be fitted into other kinetic models.

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