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Development Of Predictive Model For Heavy Metals In Soil Of Lagos State University, Lagos State, Nigeria Using Response Surface Design

*[1]Salami, L. and [2]Adesokan, A.
[1]Environmental Engineering Research Unit, Department of Chemical Engineering, Lagos State University, Epe, Lagos State, Nigeria
[2]Department of Chemical Engineering, Lagos State University, Epe, Lagos State, Nigeria
*Corresponding author: SalamiLukumon@yahoo.com; Lukumon.salami@Lasu.edu.ng

ABSTRACT
Predictive models are veritable tools for estimation of heavy metals in soil for the purpose of decision making. The development of predictive models for heavy metals in soil of Lagos State University (LASU), Epe, Lagos State, Nigeria using response surface design was carried out. Response surface methodology (RSM) was used to design the experiment using one factor design modeling technique of design expert version 10.0.3 Software. Soil samples were taken at various distances (0, 0.25, 050, 0.75 and 1.00 m) which were stored in different polythene bags labeled SK1 – SK5. The soil samples were analysed in the laboratory for copper (Cu), iron (Fe), zinc (Zn), cadmium (Cd), chromium (Cr) and lead (Pb) with the aid of Atomic Absorption Spectrophotometer (Model 210 VGP). Analysis was carried out on the experimental data using the design expert version 10.0.3 Software to obtain predictive models and coefficient of determination (R^2). The results revealed that the concentrations of Cu, Fe and Zn varied between 2.95 and 152.44 mg/kg, between 0.09 and 124.60 mg/kg and between 0.0011 and 101.75 mg/kg respectively while Mn and Pb ranged between 0.11 and 177.06 mg/kg and between 1.14 and 119.78 mg/kg. the concentrations of cadmium and chromium were less than 0.001 mg/kg. The R^2 values obtained for linear, quadratic, cubic and quartic models varied between 0.001 and 0.0064, between 0.2373 and 0.2622, between 0.2509 and 0.2869 and 1.000 respectively. Hence quartic models were accepted bout linear, quadratic and cubic models were ignored. The predictive models developed predicted the experimental data perfectly which implied that the predictive models developed were good representation of heavy metals in LASU soil matrix.

***KEYWORDS**: Development, heavy metals, Lagos State University, model, predictive, response surface and soil.*

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I. INTRODUCTION

Soil polluted by heavy metals constitutes a threat to the environment and public health. Heavy metals occur naturally in the soil however anthropogenic sources such as accidental spills, chemical leaks, burning of fossil fuel and inappropriate disposal of wastes have increased the concentrations of heavy metals in soil resulting in soil pollution (Rajaganapathy, 2011 and Owoso *et al.*, 2007). The accumulation of heavy metals in soils is a concern due to food security issues (McLaughlin *et al.*, 1999). The understanding of heavy metals source can aid in targeting actions to reduce human exposure and improve the quality of the environment (Steeve, 2010).

Several works have been done on soil contamination and pollution (Lim et al., 2008; Wuana and Okieimen, 2011; Rizo et al., 2012; Muirhead, 2009; Shishov *et al*., 2004; Salami and Susu, 2016; Odunlami and Salami, 2017; Chukwu etal., 2018; Iyama and Edori, 2020; Ahmad et al., 2016; Dada and Aruwa, 2014; Carlos *et al*., 2012 and Adeniyi and Afolabi, 2002; Nwankwoala *et al*., 2018; Juan et al., *2016*; Owoso *et al.*, 2017; Olatunde *et al*., 2018; Fatai *et al*., 2019 and Ugwu and Ofomoh, 2021). Juan *et al.* (2016) carried out entropy – cloud model of heavy metals pollution assessment in farmland soils of mining areas. The work provided a new way to assess soil heavy metal pollution which is different from other methods like fuzzy sets, artificial neural network and normal cloud model. Owoso *et al.* (2017) investigated heavy metals contamination of soil and groundwater by artisanal activities in Lagos metropolis, Nigeria. The investigation showed a very high degree of contamination of soil and groundwater which was an indication of serious anthropogenic pollution from artisanal activities at the location.

Olatunde *et al*. (2018) worked on exposure of heavy metals in soil and dust from playground and classroom in selected primary schools in Lagos State, Nigeria. The work revealed that there was exposure to some heavy metals in soil and dusts from playground via ingestion pathway which was of greatest carcinogenic risk. Fatai *et al.* (2019) examined sources and pattern of heavy metals concentrations in urban road dusk, Lagos metropolis. The examination identified anthropogenic activities as the major source of metal pollution in the studied road dusk. Broomandi *et al.* (2020) worked on critical review of soil contamination in areas impacted by military activities. The work showed that heavy metals have been found in elevated concentrations in many military impacted zones. Ugwu and Ofomoh, (2021) assessed the health risk of students' exposure to some potentially toxic metals in classroom dust in Southeast. Nigeria. The assessment proved that there was carcinogenic risk for ingestion of dust.

Many approaches have been used to assess the pollution of soil. It can be assessed either by the experimental determination of heavy metals or their estimation through mathematical modeling (Hudak, 1998; Stoline *et al*., 1993; Moo-Young *et al.*, 2004 and Salami and Susu, 2015). Therefore the aim of the work is to development predictive models for heavy metals in soil of LASU, Epe, Lagos State, using response surface design.

Response surface methodology (RSM) is a mathematical tool which aids in better understanding of response of an experiment by feeding the software with information which eventually provides an accurate prediction response (Alaya – Ibrahim *et al.*, 2018). RSM has numerous advantages over conventional method (Alaya – Ibrahim *et al.*, 2018). These include: ability to estimate the interactions between the process parameters, it reduces cost of analysis associated resources and process development and it efficiently predict values from numerical or practical experiments at discrete point. RSM is a useful technique for predictive modeling (Edozium *et al*., 2018). The development of a predictive model for heavy metals in soil of LASU will help to estimate the concentrations of heavy metals at various depths in soil of LASU which justifies this noble work.

II. METHODOLOGY

2.1 Experimental Design

RSM was used to design the experiment using one factor design modeling technique of design expert version 10.0.3 software. 5 experimental runs were generated for the one factor design. One factor design was chosen in order to study the concentrations of heavy metals at various depths. The summary of the design parameters were shown in Table 1. The minimum and maximum depict the lowest and highest values used in the design of the experiment.

Table 1. Summary of the parameters employed for the experimental design

Factor	Unit	Minimum	Maximum
Depth (m)	m	0.00	1.00

2.2 Soil Sampling

Soil sample was taken during the month of October, 2020 from surface layer (0 m) soil of LASU, Epe with the aid of stainless auger. The sample was stored in a polythene bags was labeled SK1. The sampling point was coordinated using handheld Global Positioning System (GPS) (Etrex 12 Garmin model). The auger was washed with distilled water. The sampling point was then dug within 6 inches diameter up to a depth of 0.25 m and soil sample was collected with the aid of the stainless auger. The sample was stored in another polythene bag labeled SK2. The sampling point was dug further up to points 0.5, 0.75 and 1.0 m where soil samples were collected and stored in various polythene bags labelled SK3 – SK5. The auger was washed each time it was used for collection of sample before using it again. All the soil samples were quickly transferred to the laboratory.

2.3 Analysis of Soil Samples

The method of Salami and Susu (2016) was used with a little modification. The soil samples were first air dried overnight in an oven at 32^oC. The dried samples were mechanically ground and sieved through 200 mesh size sieve to remove large debris, gravel sized materials and plant roots. 5 g of each sieved samples was placed in an Erlenmeyer flask and 2.5 ml of extracting solution (0.05N HCl + 0.24 H_2SO_4) was added after which the mixture was placed in a mechanical shaker for 20 minutes as compared to 15 minutes used by Salami and Susu (2016). The resulting solution was filtered through whatmann filter paper into a 50 ml volumetric flask and diluted to 50 ml with the extracting solution. The treated samples were analysed for the following heavy metals: Cu, Fe, Cd, Cr, Mn and Pb using Atomic Absorption Spectrophotometer (Model 210 VGP).

2.4 Statistical Analysis and Modeling of Heavy Metals

Analysis was carried out on the experimental data using design expert version 10.0.3 software to obtain models and the coefficient of determination that is goodness fit (R^2). The sampling point was assumed to be a homogeneous porous medium and isotropic saturated.

III. RESULTS AND DISCUSSION

The experimental design and response factor for the concentrations of heavy metals in soil of LASU, Epe, Lagos State is presented in Table 2 while the model summary statistics of heavy metals in soil of LASU is depicted in Table 3. The coordinates of the sampling point were 06° 35.659'N and 003° 59.850'E. The predictive models were shown in Equations 1 – 5 for copper, iron, zinc, manganese and lead respectively. Cadmium and chromium were ignored because their concentrations were less than 0.001 mg/kg.

Table 2. Experimental design and response factor for the concentrations of heavy metals in soil of LASU, Epe, Lagos State

Experimental runs	Depth (m)	Concentrations of heavy metals (mg/kg)				
		Cu	Fe	Zn	Mn	Pb
1	0	4.86	3.62	2.17	3.37	4.23
2	0.25	118.17	124.60	101.75	120.41	119.78
3	0.50	6.89	5.54	4.62	2.73	3.66
4	0.75	152.44	101.02	95.59	177.06	139.65
5	1.00	2.95	0.09	0.001	0.11	1.14

Table 3. Model summary of statistics of heavy metals in soil of LASU, Epe, Lagos State

Source	R^2				
	Cu	Fe	Zn	Mn	Pb
Linear	0.0044	0.0064	0.0010	0.0092	0.0010
Quadratic	0.2501	0.2611	0.2622	0.2373	0.2414
Cubic	0.2737	0.2740	0.2632	0.2869	0.2509
Quartic	1.000	1.000	1.000	1.000	1.000

In Table 3, the concentrations of copper and iron varied between 2.95 and 152.44 mg/kg and between 0.09 and 124.60 mg/kg respectively. The concentrations of zinc and manganese ranged between 0.0011 and 101.75 mg/kg and between 0.11 and 177.06 mg/kg respectively while that of lead varied between 1.14 and 119.78 mg/kg. The reference values used for evaluating concentrations of potentially toxic elements in soil for copper were 28 mg/kg (US) (Denton *et al*., 2016), 45 mg/kg (Spain) (Rodriguez – Seijo *et al*., 2016) and 65 mg/kg (Bosnia) (Tomic *et al*., 2018), that of zinc were 150 mg/kg (Bosnia) (Tomic *et al*., 2018), 46 mg/kg (US) (Denton *et al*., 2016) and 500 mg/kg (Spain) (Rodriguez – Seijo *et al*., 2016) while lead were 80 mg/kg (Bosnia) (Tomic *et al*., 2018), 46 mg/kg (US) (Denton *et al*., 2016) and 100 mg/kg (Spain) (Rodriguez – Seijo *et al*., 2016). This revealed the concentrations of heavy metals in soil of LASU were below the reference values for evaluating the concentrations of potentially toxic elements in aforementioned countries.

LASU, Epe, Lagos State was a formal military barrack before it was converted to a university campus. Chemicals particularly non – biodegradable elements and compounds used in military ammunition and explosives are likely to contaminate soil which may later cause detrimental impacts on human health and large ecosystem around the world (Lima *et al*., 2011; Poesen, 2017 and Broomandi *et al*., 2020). The concentrations of heavy metals in soil of LASU were likely not to cause any detrimental impacts on human health and ecosystem. This is an indication that the activities of the military have not impacted negatively on the soil of LASU.

In Table 3, the goodness fit values which is also known as coefficient of determination (R^2) for linear and quadratic models ranged between 0.0010 and 0.0064 and between 0.2373 and 0.2622 respectively while that of cubic and quartic models varied between 0.2509 and 0.2869 and 1.000 respectively. The higher the goodness fit value, the better and more accurate the predictive models. Based on the goodness fit values obtained for linear, quadratic, cubic and quartic models, quartic models have the goodness fit value of unity hence quartic models presented in Equations 1 – 5 were accepted but linear, quadratic and cubic models were jettison.

$$Cu = 4.86 + 2577.6033 A - 13225.54 A^2 + 21667.78 A^3 - 11021.76 A^4 \tag{1}$$

$$Fe = 3.62 + 2435.6367 A - 11904.18 A^2 + 18697.33 A^3 - 9232.32 A^4 \tag{2}$$

$$Zn = 4.62 - 7.85 A + 502.78 A^2 + 6.77 A^3 - 506.31 A^4 \tag{3}$$

$$Mn = 3.37 + 2809.9267 A - 1471.7467 A^2 + 24338.7733 A^3 - 12480.2133 A^4 \tag{4}$$

$$Pb = 4.23 + 2580.97A - 13133.12667A^2 + 21326.56A^3 - 10777.4933A^4 \quad (5)$$

The developed predictive models shown in Equations 1 – 5 for Cu, Fe, Zn, Mn and Pb respectively were used to predict the concentrations of heavy metals at various depths to obtain predictive values. The predictive values were plotted against the actual values and the graphs depicted in Figures 1 – 5 were generated for Cu, Fe, Zn, Mn and Pb respectively. The graphs showed a perfect relationship between the predicted and the experimental data. This implied that the developed predictive models were good representation of the heavy metals in soil matrix of LASU.

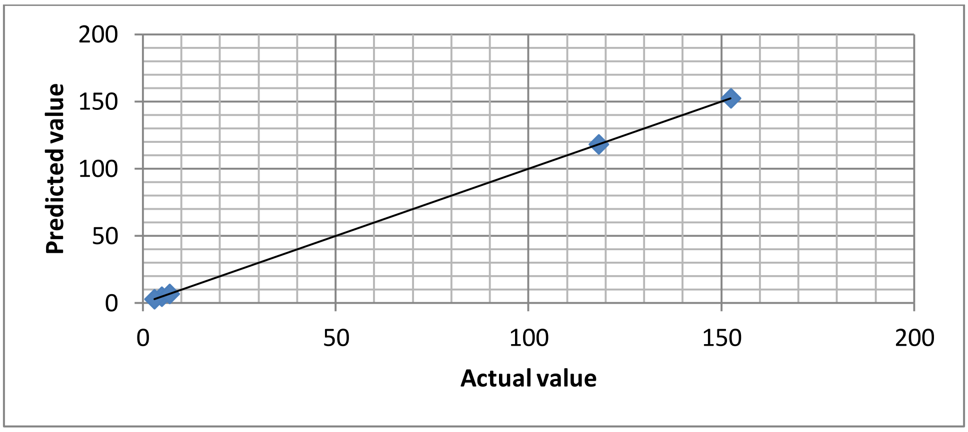

Fig. 1. A graph of predicted against actual value for copper

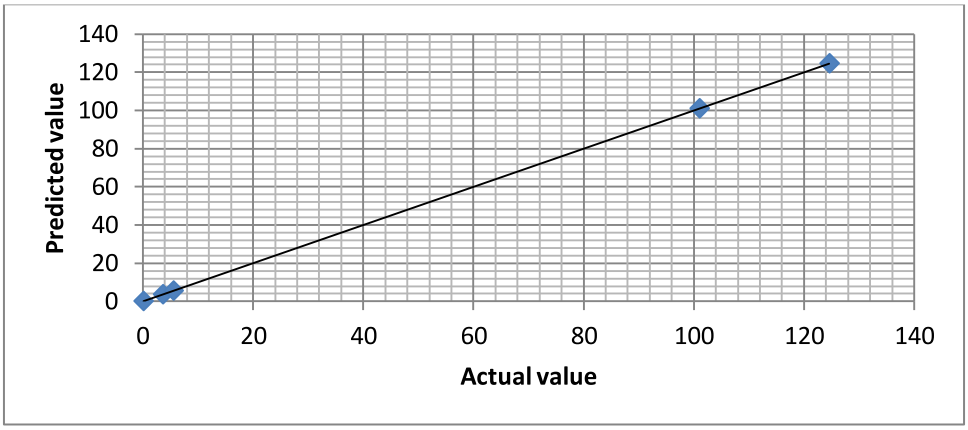

Fig. 2. A graph of predicted against actual value for iron

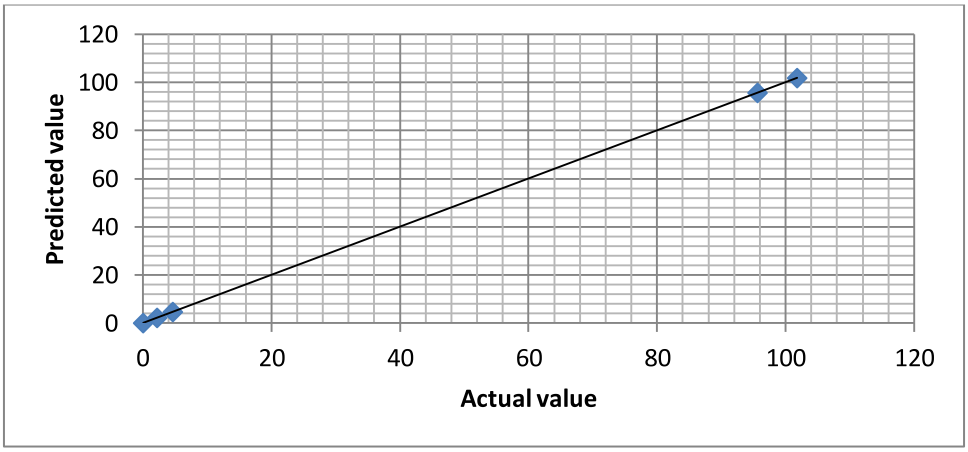

Fig. 3. A graph of predicted against actual value for zinc

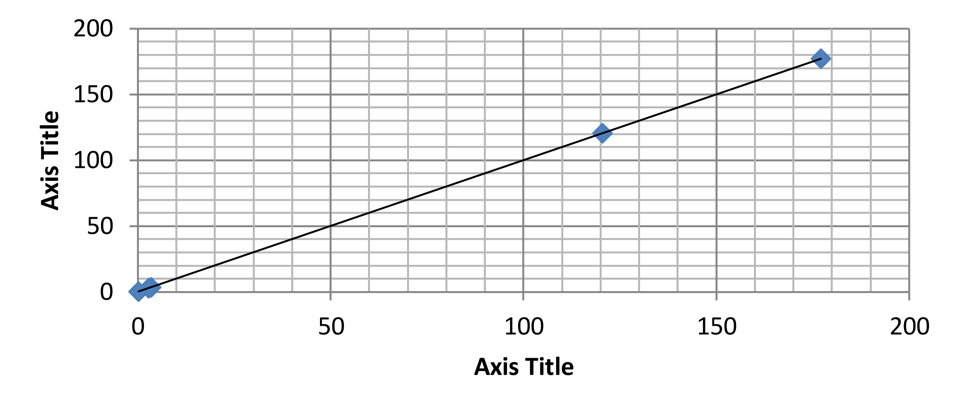

Fig. 4. A graph of predicted against actual value for manganese

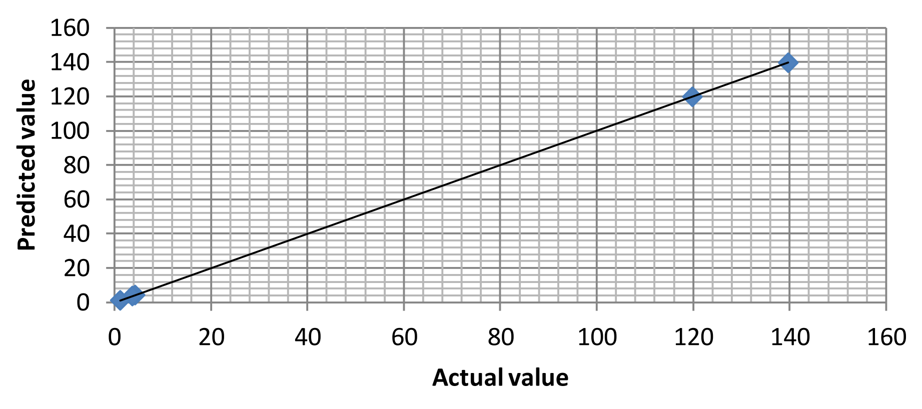

Fig. 5. A graph of predicted against actual value for lead

IV. CONCLUSION

Predictive models for heavy metals in soil of LASU, Lagos State, Nigeria have been developed. The concentrations of copper, iron and zinc ranged between 2.95 and 152.44, between 0.09 and 124.60 and between 0.0011 and 101.75 mg/kg respectively while that of manganese and lead varied between 0.11 and 177.06 and between 1.14 and 119.78 mg/kg respectively. Linear, quadratic, cubic and quartic predictive models were developed and various goodness fit values (R^2) were considered. The quartic predictive models have goodness fit of unity and on this basis, linear, quadratic and cubic predictive models were rejected but the quartic predictive models were accepted for Cu, Fe, Zn, Mn and Pb. The quartic predictive models developed were used to predict the experimental data. A very good correlation existed between the experimental and predicted data which implied that the developed predictive models were good representation of the heavy metals in LASU soil matrix.

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