Chemistry and Materials Research ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online) Vol.7 No.11, 2015



Experimental Optimization of Lead (II) Bioadsorption from Aqueous Solution onto Banana Stalk using Central Composite Design

Ogunleye, O. O. Ajala, M. A. Agarry, S. E. Agbede, O.O.

Department of Chemical Engineering, Ladoke Akintola University of Technology, P. M. B. 4000, Ogbomoso -

Nigeria

Abstract

This study investigated the effect of operating parameters on the bioadsorption process of Pb(II) from its aqueous solution using three Banana Stalk (BS) bioadsorbents [Raw (RBS), Acid Activated (AABS) and Base Activated (BABS)]. A five-factor, three-level Central Composite Design (CCD) was applied to determine the effects of independent variables (initial metal concentration, contact time, temperature, adsorbent dosage and solution pH) on percentage Pb(II) removal. Response Surface Methodology (RSM) was employed to optimize the parameters in the experiment. AABS had the highest percentage removal (96.13%) from the preliminary experiment and was then used for the optimisation experiment. Data analysis showed that all the variables significantly affected the percentage Pb(II) removal at p < 0.05. The square of the adjusted coefficient of determination for regression model of percentage Pb(II) removal is 0.9355. Optimum percentage removal of 96.41% was obtained using AABS when the Pb(II) concentration, contact time, temperature, dosage and solution pH were 21.83g/mL, 152.21minutes, 50°C, 0.90g and 8.00, respectively. There absolute error between the experimental and the predicted optimum percentage removal was less than 1%. **Keywords:** Banana stalk, optimization, bioadsorption, acid, base.

1. Introduction

Several human diseases and other health hazards had been attributed to exposure to Lead beyond the World Health Organisation (WHO) maximum permissible limit (Needleman 1999; Pruss-Ustun *et al.*, 2004; WHO 2000; Wang 2002; dos Santos *et al.*, 2011). Among these health hazards is the formation of complexes with oxogroups in enzymes which in turns inhibits the process of haemoglobin synthesis and porphyrin metabolism (Ademorati 1996). Lead bearing wastewater is on the increase due to enhanced industrialization such as manufacturing of storage batteries, television tube, printing, paints, pigments, photographic materials, gasoline additives, matches and explosives (Axtell *et al.*, 2003; Bhatti *et al.*, 2007; Qiu *et al.*, 2008).

One of the well know effective and economical method of treatment of Lead polluted water is biosorption. It is based on metal binding capacities of various biological materials mainly composed of cellulose, hemicelluloses and lignin that make them effective adsorbents for a wide range of pollutants due to the presence of functional groups such as hydroxyl, carboxyl, methoxyl and phenols (Abdel- Ghani *et al.*, 2007; Babarinde *et al.*, 2006; Dermirbas, 2008; Ajmal *et al.*, 2000; Hassanein and Koumanova, 2012). Many plant materials have been used to remove heavy metals from their solution. These include empty palm oil fruit bunch (Rafeah *et al.*, 2009), soursop seeds (Oboh and Aluyor 2008), modified cassava fibre (Egila and Okorie 2002), coconut shell (Gimba *et al.*, 2001) and duck weed (Upatham *et al.*, 2002), sago waste (Ho *et al.*, 2002), african spinach stalk (Egila *et al.*, 2011), palm fruit fibre (Bello *et al.*, 2011), hop (Gardea-Torresdey *et al.*, 2002) orange peels (Li *et al.*, 2007;Liang *et al.*, 2009a, Liang *et al.*, 2009b) and spent tea leaves (Amir *et al.*, 2005; Agarry *et al.*, 2013).

However, some process conditions, such as temperature, pH, pollutant concentration, stirring speed, contact time, particle size, the physical-chemical properties of bioadsorbent are very significant factors that determine the performance of bioadsorption processes (Sarkar and Majumder, 2011; Kumar *et al.*, 2013 and Mahmood *et al.*, 2014). The interactions of these factors are complex and understanding them can lead to optimal operation of the process. One major statistical tool for analysing complex process systems and establishing optimum conditions within the design space is Response Surface Methodology (RSM). It is a collection of mathematical and statistical approach for experimental design useful for analyzing and evaluating the effects of several independent variables and also interactive effects among the variables on the response. It also has an important application for searching optimum conditions of variable to predict targeted responses (Kiran *et al.*, 2007;Tsai *et al.*, 2010 and Fereidouni *et al.*, 2009).

Banana (*Musa paradisiaca*) Stalk (BS) is a rich lignocellulosic agricultural waste whose previous application has been limited to the production of activated carbon for malachite green dye removal (Bello *et al.*, 2012). Raw and modified (acidic and basic) BS based bioadsorbent are produced in this present study and used to investigate the interactive effects of adsorbent dose, temperature, initial Pb(II) concentration, contact time and pH on the percentage Pb(II) removal using RSM. Empirical model correlating response to the five independent variables was then developed and optimization of process conditions for Pb(II) bioadsorption was determined using Central Composite Design (CCD).

2. Materials and Method

2.1 Preparation and Characterization of Adsorbents

Banana Stalks (BS) was sundried, cut into small pieces and washed with distilled water to remove dirt particles. BS pieces were then dried in the oven at 100 $^{\circ}$ C for 24 hours to constant weight before being grounded and screened to 300 - 425µm mesh particle size. It was then stored as Raw Banana Stalk (RBS). RBS of 200g was soaked with 1M H₃PO₄ in ratio 1:1, kept in the oven for 24hours at 80°C for activation and stored as Acid Activated Banana Stalk (AABS). Similarly, Base Activated Banana Stalk (BABS) was prepared by soaking another 200g of the RBS in 0.1M KOH for 24 hours at 80°C in an oven and stored as BABS. Proximate analysis of the biosorbents was carried out to know the percentage compositions of its constituents. Fourier Transform Infrared (FTIR) spectroscopic analysis was performed on RBS, AABS and BABS using FTIR-2000, Perkin– Elmer. The spectra were measured from 4000 to 400 cm⁻¹.

2.2 Preparation of Pb(II) Solution

Solution containing Pb (II) was prepared from Pb(NO₃)₂ of 1000 mgL⁻¹ stock solutions. Reagents used were of analytical grade and deionized water was used in solution preparation. Other concentrations (20 - 100 mg/L) were obtained from this stock solution by serial dilution. Fresh dilutions was used for each experiment. The concentration of Pb(II) in simulated wastewater was analysed by Atomic Absorption Spectrophotometer (model Pye Unicam SP-9 Cambridge, UK.)

2.3 Batch Biosorption Experiment

Batch biosorption tests were carried out on Pb(II) solution using RBS,AABS and BABS. The effect of adsorbent dose, temperature, initial lead ion concentration, contact time and pH were investigated. Preliminary batch experiments was conducted on AABS, BABS and RBS at an initial lead ion concentration of 100 mgl⁻¹, temperature of 30°C, pH of 7 and adsorbent mass of 1g for a total experimental time of 360 minutes to select the best biosorbent out of the three in terms of percentage Pb(II) removal for the purpose of optimisation studies. In order to evaluate the percentage Pb(II) removal, sample solutions were withdrawn at the set time interval to determine residual concentrations. Solutions were filtered prior to analysis in order to minimise the interference of the RBS. The linear Beer–Lambert relationship between absorbance and concentration with the calibration curve was established by plotting the graph of absorbance versus concentration of the lead solution. The concentration of lead solution before and after adsorption was determined. This experiment was done in turns for AABS and BABS. The percentage Pb(II) removal was calculated using Equation (1):

Removal (%) =
$$\frac{C_o - C_t}{C_o} X 100\%$$

(1)

Where, Co and Ct are the initial and the final lead concentration (mg/L), respectively.

2.4 Experimental Design and data Analysis

The dependent variable selected for this study was the percentage lead ion removal (Y) and the independent variables chosen were the Adsorbent dose (A), temperature (B), initial metal ion concentration (C), time (D) and pH (E). Central Composite Design (CCD) of the Responses Surface Methodology (RSM) in the Design Expert 6.8.0 version was used to design three levels experiment for these five factor. Regression analysis of the experimental data to fit the response equation in terms of the factors was carried out and the quality of fit of the model was expressed by the correlation coefficient (R-squared) and Analysis of Variance (ANOVA). A second order polynomial equation was proposed to fit the experimental data as given in equation (2):

$$Y = a_{0} + a_{1}A + a_{2}B + a_{3}C + a_{4}D + a_{5}E + a_{11}A^{2} + a_{22}B^{2} + a_{33}C^{2} + a_{44}D^{2} + a_{55}E^{2} + a_{12}AB + a_{13}AC + a_{14}AD + a_{15}AE + a_{23}BC + a_{24}BD + a_{25}BE + a_{34}CD + a_{35}CE$$
(2)
+ $a_{45}DE$

where a_0 is the value of the fitted response at the centre point of the design, a_i , a_{ij} , a_{ij} being the linear, quadratic, and cross product terms, respectively. The factors that are not significant at p<0.05 were removed from Equation (2) after the regression analysis to obtain a reduced version that was used for statistical optimisation using CCD in the design expert 6.0. 8 software of Stat-Ease Inc., Minneapolis, USA.

A statistical optimization of the model was conducted using the RSM. The CCD was used to determine the main and interaction effects of all the process parameters. The ranges of all the factors studied both in actual and coded levels are as given in Table 1. The batch equilibrium set-up was used for the combinations of factors as shown on Table 2. The resulting percentage lead ion removal using equation (1) was used to estimate the response. The actual values of the process variables and their ranges were selected based on the preliminary experiments. The optimum values of all the variables were obtained by solving the regression equations and by analyzing the contour and 3D surface plots.

Table1: Range of levels for parameters used in the adsorption capacity test

| | R | Range of levels | | | |
|---|-----|-----------------|-----|--|--|
| Parameters | -1 | 0 | +1 | | |
| A: Adsorbent dosage (g/100ml) | 0.2 | 0.6 | 1.0 | | |
| B : Temperature (°C) | 30 | 40 | 50 | | |
| C: Initial lead ions concentration (mg/l) | 20 | 60 | 100 | | |
| D : Contact time (minutes) | 30 | 105 | 180 | | |
| E: Solution pH | 4 | 6 | 8 | | |

Table 2: CCD matrix for the experimental runs

| Run | A: Adsorbent | B:Temperature | C:Initial Concentration | D:Time | E: |
|-----|--------------|---------------|-------------------------|--------|------|
| | Dose (g) | (°C) | (mg/l) | (min) | pН |
| 1 | 0.20 | 30.00 | 20.00 | 30.00 | 4.00 |
| 2 | 1.00 | 30.00 | 20.00 | 30.00 | 4.00 |
| 3 | 0.20 | 50.00 | 20.00 | 30.00 | 4.00 |
| 4 | 1.00 | 50.00 | 20.00 | 30.00 | 4.00 |
| 5 | 0.20 | 30.00 | 100.00 | 30.00 | 4.00 |
| 6 | 1.00 | 30.00 | 100.00 | 30.00 | 4.00 |
| 7 | 0.20 | 50.00 | 100.00 | 30.00 | 4.00 |
| 8 | 1.00 | 50.00 | 100.00 | 30.00 | 4.00 |
| 9 | 0.20 | 30.00 | 20.00 | 180.00 | 4.00 |
| 10 | 1.00 | 30.00 | 20.00 | 180.00 | 4.00 |
| 11 | 0.20 | 50.00 | 20.00 | 180.00 | 4.00 |
| 12 | 1.00 | 50.00 | 20.00 | 180.00 | 4.00 |
| 13 | 0.20 | 30.00 | 100.00 | 180.00 | 4.00 |
| 14 | 1.00 | 30.00 | 100.00 | 180.00 | 4.00 |
| 15 | 0.20 | 50.00 | 100.00 | 180.00 | 4.00 |
| 16 | 1.00 | 50.00 | 100.00 | 180.00 | 4.00 |
| 17 | 0.20 | 30.00 | 20.00 | 30.00 | 8.00 |
| 18 | 1.00 | 30.00 | 20.00 | 30.00 | 8.00 |
| 19 | 0.20 | 50.00 | 20.00 | 30.00 | 8.00 |
| 20 | 1.00 | 50.00 | 20.00 | 30.00 | 8.00 |
| 21 | 0.20 | 30.00 | 100.00 | 30.00 | 8.00 |
| 22 | 1.00 | 30.00 | 100.00 | 30.00 | 8.00 |
| 23 | 0.20 | 50.00 | 100.00 | 30.00 | 8.00 |
| 24 | 1.00 | 50.00 | 100.00 | 30.00 | 8.00 |
| 25 | 0.20 | 30.00 | 20.00 | 180.00 | 8.00 |
| 26 | 1.00 | 30.00 | 20.00 | 180.00 | 8.00 |
| 27 | 0.20 | 50.00 | 20.00 | 180.00 | 8.00 |
| 28 | 1.00 | 50.00 | 20.00 | 180.00 | 8.00 |
| 29 | 0.20 | 30.00 | 100.00 | 180.00 | 8.00 |
| 30 | 1.00 | 30.00 | 100.00 | 180.00 | 8.00 |
| 31 | 0.20 | 50.00 | 100.00 | 180.00 | 8.00 |
| 32 | 1.00 | 50.00 | 100.00 | 180.00 | 8.00 |
| 33 | 0.20 | 40.00 | 60.00 | 105.00 | 6.00 |
| 34 | 1.00 | 40.00 | 60.00 | 105.00 | 6.00 |
| 35 | 0.60 | 30.00 | 60.00 | 105.00 | 6.00 |
| 36 | 0.60 | 50.00 | 60.00 | 105.00 | 6.00 |
| 37 | 0.60 | 40.00 | 20.00 | 105.00 | 6.00 |
| 38 | 0.60 | 40.00 | 100.00 | 105.00 | 6.00 |
| 39 | 0.60 | 40.00 | 60.00 | 30.00 | 6.00 |
| 40 | 0.60 | 40.00 | 60.00 | 180.00 | 6.00 |
| 41 | 0.60 | 40.00 | 60.00 | 105.00 | 4.00 |
| 42 | 0.60 | 40.00 | 60.00 | 105.00 | 8.00 |
| 43 | 0.60 | 40.00 | 60.00 | 105.00 | 6.00 |

3. Results and Discussion

3.1 Characterisation of Biosorbent

The result of proximate analysis and FTIR carried out on the biosorbent samples are as presented in preliminary experiment of Ogunleye *et al.* (2014) are as presented on Table 3 and 4, respectively. The AABS, BABS and RBS are rich in crude fibre that comprise of lignin, cellulose and hemicellulose content. Lignin is a compound rich with functional groups, such as carbonyl, ether and hydroxyl (Abdel-Ghani et al., 2007). The implication of these is that the presence of these active site presupposes that banana stalks are good biosorbents. The FTIR spectra characteristics for the three biosorbents presented on Table 4 revealed that the biosorbents are rich in hydroxyl, carboxyl and the phenolic groups which indicates that RBS, AABS and BABS are viable for the adsorption of Pb(II) onto the biosorbents.

| Table 3 P | Table 3 Proximate analysis of banana stalks | | | | | | | |
|-----------|---|-------------|-------------|-------------|------------------|--|--|--|
| Sample | Moisture | Ash content | Crude fibre | Protein (%) | Carbohydrate (%) | | | |
| | content (%) | (%) | (%) | | | | | |
| AABS | 10.38 | 5.52 | 67.69 | 6.29 | 10.12 | | | |
| BABS | 10.88 | 5.93 | 62.07 | 7.93 | 13.26 | | | |
| RBS | 12.19 | 7.40 | 58.47 | 8.58 | 14.10 | | | |

| IR peak | Band wave number(cm ⁻¹) | | er(cm ⁻¹) | Assigned functional group |
|---------|-------------------------------------|---------------|-----------------------|---|
| | RBS | RBS BABS AABS | | |
| 1 | 3889.63 | 3287.10 | 3327.12 | O-H stretching vibration of alcohol or carbonyl acid. |
| 2 | 2918.26 | 2920.86 | 2918.94 | C-H stretching vibration of alkane. |
| 3 | 2184.23 | 2541.21 | 2209.05 | C-H stretching of alkyne |
| 4 | 1916.51 | | | C-O stretching vibration of alkene and ketones. |
| 5 | 1636.18 | 1604.94 | 1628.34 | C-H stretching of alkene |
| 6 | 1029.54 | 897.33 | 660.63 | CH bending vibration of C-H ₂ and C-H ₃ (finger print region) |

3.2 Preliminary Biosorption Experiment.

The preliminary batch experiments conducted on AABS, BABS and RBS at an initial lead ion concentration of 100 mgl⁻¹, temperature of 30°C, pH of 7 and adsorbent mass of 1g for 360 minutes is as shown on Table 5. At the total time of 360 minutes, the AABS had the highest percentage Pb(II) removal of 96.13% when compared to BABS and RBS, having 66.90% and 63.97%, respectively. This difference in the Pb(II) removal of these three biosorbents must have been due to the differences in the functional groups dominant in each of them which can be said to favour AABS in this study. Therefore, from this preliminary study, conclusion can be made that AABS was the best biosorbent from AABS, BABS and RBS considered, and hence AABS was chosen for the optimization study.

| Adsorbent | Initial conc. (mgL ⁻¹) | Time (min) | рН | Adsorbent dose (g) | Final conc. (mgL ⁻¹) | Removal of Pb (II) (%) |
|-----------|---------------------------------------|------------|----|--------------------|-------------------------------------|------------------------|
| AABS | 100 | 60 | 7 | 1 | 11.63 | 88.4 |
| AABS | 100 | 120 | 7 | 1 | 5.62 | 94.4 |
| AABS | 100 | 180 | 7 | 1 | 3.93 | 96.1 |
| AABS | 100 | 240 | 7 | 1 | 3.89 | 96.11 |
| AABS | 100 | 300 | 7 | 1 | 3.87 | 96.13 |
| AABS | 100 | 360 | 7 | 1 | 3.87 | 96.13 |
| BABS | 100 | 60 | 7 | 1 | 56.80 | 43.2 |
| BABS | 100 | 120 | 7 | 1 | 42.99 | 57.0 |
| BABS | 100 | 180 | 7 | 1 | 34.23 | 65.77 |
| BABS | 100 | 240 | 7 | 1 | 33.13 | 66.87 |
| BABS | 100 | 300 | 7 | 1 | 33.13 | 66.87 |
| BABS | 100 | 360 | 7 | 1 | 33.10 | 66.90 |
| RBS | 100 | 60 | 7 | 1 | 47.43 | 52.57 |
| RBS | 100 | 120 | 7 | 1 | 37.77 | 62.2 |
| RBS | 100 | 180 | 7 | 1 | 37.12 | 62.8 |
| RBS | 100 | 240 | 7 | 1 | 36.12 | 63.88 |
| RBS | 100 | 300 | 7 | 1 | 36.03 | 63.97 |
| RBS | 100 | 360 | 7 | 1 | 36.03 | 63.97 |

Table 5 Adsorption performance of AABS, BABS and RBS.

3.3 Batch Biosorption of Pb(II) using AABS

The percentage Pb(II) removal from the batch experiment and the predicted values using AABS based on the CCD design in Table 2 is as presented on Table 6. At each pair of run of the experiment, runs 1 and 5; 2 and 6; 25 and 29; 26 and 30; 37 and 43 had the same process conditions with different initial Pb (II) concentration; results shows that percentage Pb(II) removal decreased with increased initial Pb(II) concentration. This trend is as a result of limited number of active sites on biosorbents which got saturated at certain concentration (Tsai and Chen, 2010; Ogunleye *et al.*, 2014). Percentage Pb(II) removal increased with increasing pH value as observed from pairs of runs 1 and 17; 2 and 18 when other condition are constant. This trend is similar for temperature as obtained from the pairs of runs 1 and 7; 2 and 8; 29 and 31; 30 and 32. The reverse in the trend of result obtained for AABS compared with known trends where removal increased with increased temperature may be due to the fact that AABS surface for adsorption has acquire the maximum energy for adsorption at lower temperatures. A similar result, in which adsorptive capacity is inversely proportional to temperature was obtained by Paresh *et al.*(2010) using a biosorbent. Lower temperature of 30°C also favoured the biosorption of Lead (II) and Nickel (II) using Pigeon peas hulls waste by Ramana *et al.* (2012). Percentage Pb(II) removal also increased with increasing adsorbent dose and contact time. When more absorbent surfaces are available for sufficient time, the percentage removal is enhanced

| Run | Percentage Pb | Percentage Pb(II) Removal | | | |
|----------|----------------|---------------------------|--|--|--|
| | Observed Value | Predicted Value | | | |
| 1 | 38.60 | 37.03 | | | |
| 2 | 46.40 | 48.80 | | | |
| 3 | 32.20 | 32.34 | | | |
| 4 | 38.60 | 44.10 | | | |
| 5 | 24.60 | 25.59 | | | |
| 6 | 36.20 | 37.36 | | | |
| 7 | 22.10 | 20.89 | | | |
| 8 | 34.60 | 32.66 | | | |
| 9 | 58.10 | 56.53 | | | |
| 10 | 62.10 | 68.30 | | | |
| 11 | 56.20 | 51.84 | | | |
| 12 | 60.80 | 63.60 | | | |
| 13 | 46.60 | 45.09 | | | |
| 14 | 58.80 | 56.86 | | | |
| 15 | 40.20 | 40.39 | | | |
| 16 | 50.40 | 52.16 | | | |
| 17 | 48.20 | 50.47 | | | |
| 18 | 58.90 | 62.24 | | | |
| 19 | 46.40 | 45.78 | | | |
| 20 | 52.40 | 57.54 | | | |
| 21 | 42.60 | 39.03 | | | |
| 22 | 52.10 | 50.80 | | | |
| 23 | 38.40 | 34.34 | | | |
| 24 | 48.40 | 46.10 | | | |
| 25 | 82.20 | 82.19 | | | |
| 26 | 96.40 | 93.95 | | | |
| 27 | 78.80 | 77.49 | | | |
| 28 | 94.30 | 89.25 | | | |
| 29 | 62.10 | 70.74 | | | |
| 30 | 88.60 | 82.51 | | | |
| 31 | 58.40 | 66.05 | | | |
| 32 | 84.20 | 77.81 | | | |
| 33 | 56.40 | 58.01 | | | |
| 34 | 68.90 | 69.77 | | | |
| 35 | 78.56 | 73.57 | | | |
| 36 | 64.80 | 68.87 | | | |
| 37 | 84.30 | 69.61 | | | |
| 38 | 52.10 | 58.17 | | | |
| 39 | 38.60 | 34.24 | | | |
| 40 | 56.40 | 59.84 | | | |
| 40 41 | 58.20 | 54.12 | | | |
| 41 42 | 64.60 | | | | |
| 42 43 | 61.80 | 73.66 63.89 | | | |

3.4 Second Order Polynomial Regression Model and Statistical Analysis

The regression coefficients, standard error of coefficients, and p-values for the significant factors in the estimation of the percentage removal of Pb(II) using AABS (Y) in terms of adsorbent dose (A), temperature (B), initial Pb(II) concentration (C), contact time (D), and solution pH (E) are listed in Table 7. The reduced model of Equation (2) comprising only the significant terms at p < 0.05 as indicated on Table 7 is equation (3)

 $Y = 63.89 + 5.88A - 2.35B - 5.72C + 12.80D + 9.77E + 7.33B^{2} - 16.85D^{2} + 3.05DE$ (3)

Equation (3) was used to predict the percentage Pb(II) removal at various process conditions and the values are on the column 3 of Table 6. Analysis of variance method was employed to further estimate the

significance and accuracy of the model. The corresponding results are presented in Table 8 where the model showed very high F value (61.63) and a very low probability value (p -value model = 0.001) for the system investigated. The experimental data can be concluded to fit well in Equation (3) for the adsorption of Pb(II) onto AABS.

The Predicted R-Squared value of 0.9255 is in agreement with the Adjusted R-Squared value of 0.9355. Adequate Precision measures the signal to noise ratio. A ratio > 4 is desirable. The ratio of 31.421 in this study indicates an adequate signal. This model can be used to navigate the design space. The coefficient of variation (CV) as the ratio of the standard error of estimate to the mean value of the observed response is a measure of reproducibility of the model, generally a model can be considered reasonably reproducible if its CV is not greater than 10 per cent. Hence, the low variation coefficient value (CV = 9.02%) obtained indicates a high precision and reliability of the experiments.

| Factors | Coefficient of Estimate | DF | Standard Error | p-Value |
|-----------------------|--------------------------------|----|-----------------------|---------|
| a 0 | 63.89 | 1 | 1.80 | 0.0001* |
| a ₁ | 5.88 | 1 | 0.87 | 0.0001* |
| a ₂ | -2.35 | 1 | 0.87 | 0.0001* |
| a 3 | -5.72 | 1 | 0.87 | 0.0109* |
| a 4 | 12.80 | 1 | 0.87 | 0.0010* |
| a 5 | 9.77 | 1 | 0.87 | 0.0001* |
| a 22 | 7.33 | 1 | 2.74 | 0.0114* |
| a 44 | -16.85 | 1 | 2.74 | 0.0001* |
| a 45 | 3.05 | 1 | 0.90 | 0.0017* |

| Table 7: Coefficients of models o | f biosorption of Pb(II) onto BSAC |
|-----------------------------------|-----------------------------------|
|-----------------------------------|-----------------------------------|

| | Table 8: ANOVA fo | or response equation | of adsorptive ca | pacity of BSAC |
|--|-------------------|----------------------|------------------|----------------|
|--|-------------------|----------------------|------------------|----------------|

| S | ource | Sum of Square | DF | Mean Square | F- Value | p-value |
|----------|-------|---------------|----|-------------|----------|---------|
| Model | | 12734.78 | 8 | 1591.85 | 61.63 | 0.0001* |
| Residual | | 878.16 | 34 | 25.83 | | |
| Total | | 13612.94 | 42 | | | |

* Significant at p < 0.05; $R^2 = 0.9588$; Adjusted $R^2 = 0.9355$; Predicted $R^2 = 0.9203$ Adequate Precision = 31.421

3.5 Process Optimization

In order to acquire the maximum percentage removal of Pb(II) using AABS, the numerical optimization function based on the CCD on Design Expert 6.0.8 version was employed to locate the values of independent variables. The desirability index of the numerical optimisation of the process variables was 1.00 within the experimental space indicated on Table 1 and the maximum percentage removal (Y) obtained was 96.41 % at A (0.90 g), B (30°C), C (21.83 mg/L), D(152.21 min) and E (8).

The 3D response surface plots based on the predictive quadratic model (Equation (3)) for the percentage Pb(II) removal were plotted and shown on Figures 1 - 10. Effects of adsorbent dose and temperature at C = 21.83 mg/L, D =152.21min and E= 8 is as shown on Figure 1. The effects of adsorbent dose with each of initial concentration, contact time and pH while other factors are kept at the optimum values are as show on Figures 2,3 and 4, respectively. Similar figures for the effect of temperature with each of initial concentration, contact time and pH when other factors are kept at optimum values are as shown on Figures 5, 6 and 7, respectively. Figures 8 and 9 depict the effects of initial concentration with each of contact time and pH, respectively. Finally, Figure 10 depicts the effect of contact time and pH on the percentage Pb(II) removal.

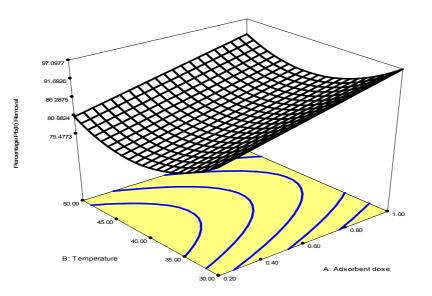


Figure 1 Effect of adsorbent dose and temperature on percentage Pb(II) removal

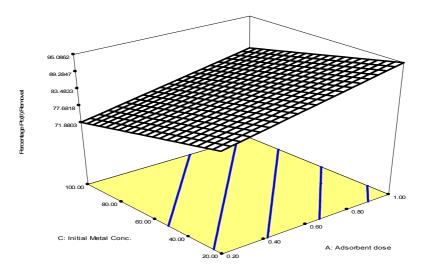


Figure 2 Effect of adsorbent dose and initial Pb(II) concentration on percentage Pb(II) removal

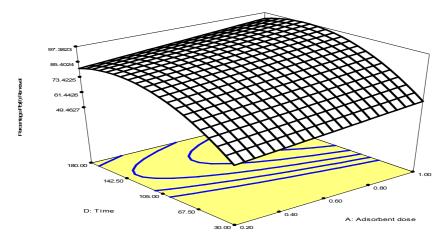


Figure 3 Effect of adsorbent dose and contact time on percentage Pb(II) removal

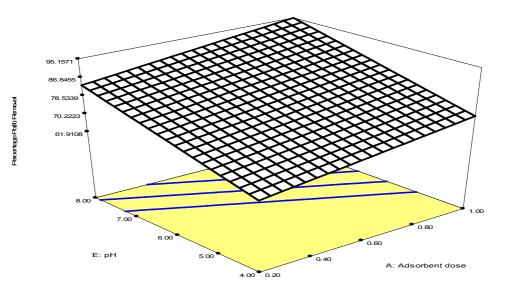


Figure 4 Effect of adsorbent dose and pH on percentage Pb(II) removal

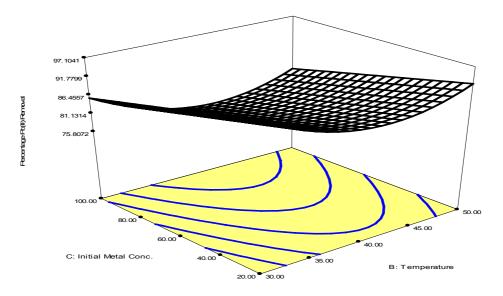


Figure 5 Effect of temperature and initial Pb(II) concentration on percentage Pb(II) removal

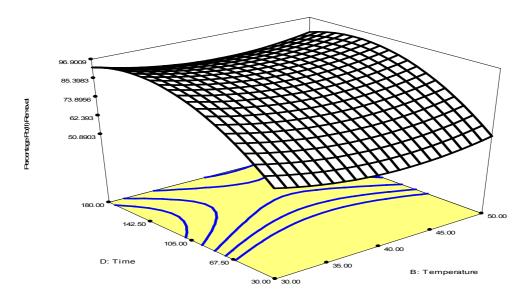


Figure 6 Effect of temperature and contact time on percentage Pb(II) removal

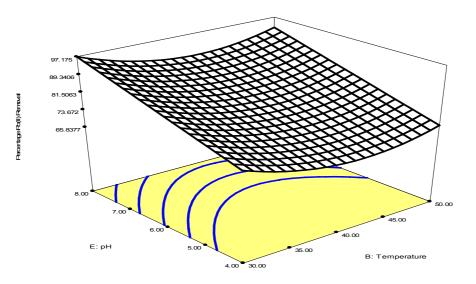


Figure 7 Effect of temperature and pH on percentage Pb(II) removal

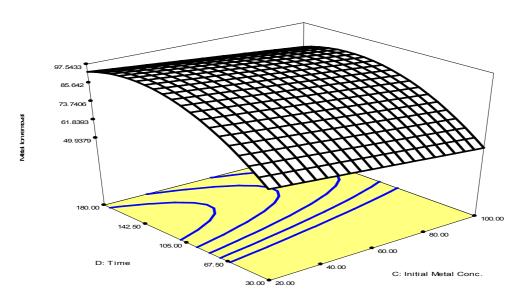


Figure 8 Effect of initial Pb(II) concentration and contact time on percentage Pb(II) removal

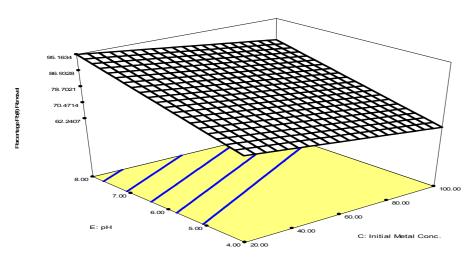


Figure 9 Effect of initial Pb(II) concentration and pH on percentage Pb(II) removal

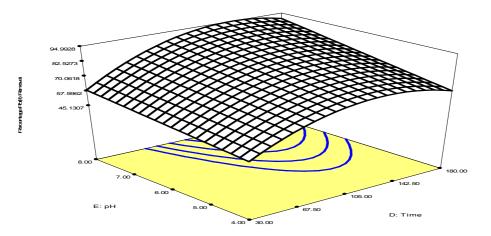


Figure 10 Effect of contact time and pH on percentage Pb(II) removal

3.6 The Validation of the Optimal Conditions

To test if the predicted optimal condition values were in line with the corresponding experimental results, additional experiments for determining percentage Pb(II) removal were performed under the optimized conditions. The initial concentration at 60, 80 and 100mg/L were imposed as constraints while other optimal conditions that would ensure maximum percentage removal were sought and experimented in triplicate and the average values compared with the predicted maximum percentage removal as shown on Table 9. The absolute relative error between the predicted and average experimented percentage removal were all less than 1%. This result shows that the model developed can be used to adequately predict the adsorption of the Pb(II) onto AABS

| C |)ptimized | l Adsorpti | on Factors | | Predicted Percentage Pb(II) Removal (%) | Experimented Percentage Pb(II) Removal (%) | Average Percentage Pb(II) Removal (%) | Absolute Relative Errors (%) |
|----------|------------|-------------|----------------|-----|---|---|--|---------------------------------------|
| A (g) | В (°С.) | C (mg/L) | D (minutes) | Е | Ypred | Y _{Exp} | Y _{Ave} . | |
| 1.00 | 31 | 60 | 150 | 8 | 91.46 | 90.60 91.80 89.90 | 90.77 | 0.76 |
| 1.00 | 30 | 80 | 140 | 8 | 90.05 | 90.20 90.10 89.70 | 90.00 | 0.06 |
| 1.00 | 30 | 100 | 130 | 7.5 | 86.94 | 87.30 86.60 87.20 | 87.03 | 0.11 |

Table 9 Validation of the optimal pparameters of Pb(II) removal using AABS

4. Conclusion

This study demonstrated efficacy of banana stalk (*Musa Paradisiaca*) as a biosorbent for removing lead ion from its solution. The experimental design method of optimization via central composite design in estimating the influence of interaction of adsorption variables on the percentage Pb(II) removal using AAABS has also been established. The initial concentration, contact time, temperature, adsorbent dose and pH had varying influences on the adsorption of Pb(II) using AABS as biosorbent. The obtained reduced second-order polynomial quadratic regression model for the percentage Pb(II) removal using AABS was significant. Finally, the maximum percentage Pb(II) removal of AABS predicted by the model was in agreement with the experimental values.

References

- Abdel-Ghani, N.T., Hefny, M., and El-Chaghaby, G.A.F. (2007). Removal of Lead from Aqueous Solution using Low-cost Abundantly Available Adsorbents. *International Journal of Environmental Science and Technology*, 4(1): 67-73.
- Ademorati, C.M.A. (1996). Environmental Chemistry and Toxicology. Pollution by Heavy Metals. Foludex Press Ibadan. 171-172.
- Agarry, S. E., Ogunleye, O.O. and Aworanti, O.A. (2013). Biosorption Equilibrium, Kinetic and Thermodynamic Modelling of Naphthalene Removal from Aqueous Solution onto Modified Spent Tea Leaves. *Journal of Environmental Technology*, 34 (7): 825-839.
- Ajmal, M., Rao, R.A.K. and Ahmad, J. (2000). Adsorption Studies on *Citrus reticulata* (Fruit Peel of Orange): Removal and Recovery of Ni (II) from Electroplating Wastewater. *Journal of Hazard Materials*, B79: 117–131.
- Amir, H.M., Darush, N., Forugh, V. and Sharokh, N. (2005). Tea Waste as an Adsorbent for Heavy Metal Removal from Industrial Wastewaters, *American Journal of Applied Sciences*, 2(1): 372–375.
- Axtell NR, Sternberg SPK, Claussen K (2003) Lead and Nickel removal using Microspora and Lemna minor. Bioresource Technology, 89(1):41-48.
- Babarinde N. A. A., Babalola J. O. and Sanni R. A. (2006). Biosorption of Lead ions from Aqueous Solution by Maize Leaf. *International Journal of Physical Sciences*, 1: 023-026.
- Bello O.S., Oladipo M.A. and Olatunde A.M. (2010). Sorption Studies of Lead Ions Onto Activated Carbon Produced from Oil-Palm Fruit Fibre. *Stem Cell*, 1(1):14-29.
- Bello, O. S., Mohd A. A. and Norhidayah Ahmad. (2012). Adsorptive Features of Banana (Musa paradisiaca) Stalk-based Activated Carbon for Malachite Green Dye Removal. *Chemistry and Ecology*, 28(2): 153-167
- Bhatti H. N., Mumtaz B., Hanif M. A.and Nadeem R. (2007). Removal of Zinc ions from Aqueous Solution using *Moringa Oleifera Lam*. (horseradish tree) biomass. *Process Biochemistry*, 42: 547-553.
- Demirbas A (2008). Heavy Metal Adsorption onto Agro-Based Waste Materials: A Review. Journal of Hazardous Materials, 157 (2):220-229
- Dos Santos WNL, Cavalcante DD, da Silva EGP, da Virgrens CF, Dias FD (2011) Biosorption of Pb(II) and Cd(II) ions by *Agave sisalana* (sisal fibre). *Microchemical Journal*, 97(2):269 -273
- Egila, J.N., Dauda, B.E.N., Iyaka, Y.A and Jimoh, T. (2011). Agricultural Waste as a Low Cost Adsorbent for Heavy Metal Removal from Wastewater. *International Journal of the Physical Sciences*, 6(8): 2152-2157.

- Egila, J.N., Okorie, E.O. (2002). Influence of pH on the Adsorption of Trace Metals on Ecological and Agricultural Adsorbents. *Journal of Chemical Society of Nigeria*, 27(2): 95-98.
- Fereidouni, M., Daneshi, A., and Younesi, H. (2009). Biosorption equilibria of binary Cd(II) and Ni(II) systems onto Saccharomyces cerevisiae and Ralstonia eutropha cells: Application of response surface methodology. *Journal of Hazardous Materials*, 168: 1437–1448.
- Gardea-Torresdey, J., Hejazi, M., Tiemann, K., Parsons, J.G., Duarte-Gardea, M., and Henning, J. (2002). Use of Hop (*Humulus lupulus*) Agricultural By-Products for the Reduction of Aqueous lead (II) Environmental Health Hazards. *Journal of Hazardous Materials*, 91: 95-112.
- Gimba, C.E., Olayemi, J.Y., Ifijeh, D.O.H. and Kagbu, J.A. (2001) Adsorption of Dyes by Powdered and Granulated Activated Carbon from Coconut Shell. *Journal of Chemical Society of Nigeria*, 26(1): 23-27.
- Hassanein TF, Koumanova B (2012) Binary mixture sorption of basic dyes onto wheat straw. Bulgarian Chemical Communication, 44(2): 131 138
- Ho, Y.S., Huang, C.T., Huang, H.W. (2002). Agricultural By-Products as a Metal Sorbent: Sorption of Copper ions from Aqueous Solution onto Tree Fern. *Process Biochemistry*, 37(5): 1421-1430.
- Kiran, B., Kaushik, A. and Kaushik, C. P. (2007). Response Surface Methodological Approach for optimizing removal of CR (VI) from Aqueous Solution using Immobilized Cyanobacterium. *Chemical Engineering Journal*, 126: 147–153.
- Kumar, K. K., Prasad, M. K., Lakshmi, G. R., and Murthy, Ch V. R. (2013). Studies on Biosorption of Cadmium on Grape Pomace using Response Surface Methodology. *Desalination and Water Treatment*, 51: 5592-5598.
- Li, X., Tang, Y., Xuan, Z., Liu, Y. and Luo, F. (2007). Study on the Preparation of Orange Peel Cellulose Adsorbents and Biosorption of Cd²⁺ from Aqueous Solution. *Separation Purification Technology*, 55: 69–75
- Liang, S., Guo, X., Feng, N. and Tian, Q. (2009a). Adsorption of Cu²⁺ and Cd²⁺ from Aqueous Solution by Mercapto-acetic Acid Modified Orange Peel, *Colloids Surface B: Biointerfaces*, 73: 10–14.
- Liang, S., Guo, X., Feng, N. and Tian, Q. (2009b). Application of Orange Peel Xanthate for the Adsorption of Pb²⁺ from Aqueous Solutions, *Journal Hazard Material*, 170: 425–429.
- Mahmood, N., Ladan, R. and Fereshteh, Z. (2014) Biosorption of copper (II) on Sargassum angostifolium C.Agardh phaeophyceae Biomass, Chemical Speciation & Bioavailability, 26:3, 176-183
- Needleman, H. L. (1999). History of lead poisoning in the world. In: Lead Poisoning Prevention and Treatment: Implementing a National Program in Developing Countries. George AM (ed.). The George Foundation, Bangalore, India.
- Oboh, O.I. and Aluyor, E.O. (2008). The Removal of Heavy Metal Ions from Aqueous Solution Using Sour Sop Seeds as Biosorbent. *African Journal of Biotechnology*, 7(24): 4508-4511.
- Ogunleye, O.O., Ajala, M.A. and Agarry, S.E. (2014) Evaluation of Biosorptive Capacity of Banana (*Musa paradisiaca*) Stalk for Lead(II) Removal from Aqueous Solution. *Journal of Environmental Protection*, 5, 1451-1465.
- Paresh,C., Sarma, N. S. and Serma, H. P.(2010). Removal of Lead(II) from Aqueous Solution using Heartwood of Areca catechu powder", Desalination, 256(1-3),16-21.
- Pruss-Ustun A, Fewtrell L, Landrigan P.J, Ayuso-Mateos J.L. (2004). Lead Exposure, In: Ezzati, M., Lopez. A.D., Rodgers, A., and Murray C.J.L. Comparative Quantification of Health Risks: Global and Regional Burden of Disease Attributable to Selected Major Risk Factors. World Health Organization, Geneva.
- Qiu Y., Cheng H., Xu C., Sheng S.D. (2008). Surface Characteristics of Crop-residue-derived Black Carbon and Lead (II) Adsorption. *Water Resource journal*, 42: 567-574.
- Rafeah, W., Ngaini, Z. and Usun Jok, V. (2009) Removal of Mercury, Lead and Copper from Aqueous Solution by Activated Carbon of Palm Oil Empty Fruit Bunch. *World Applied Science Journal*, 5: 84-91.
- Ramana, D. K. V.; Reddy, H. H. K.; Yu J. S. and Seshaiah, K. (2012) . Pigeon Peas Hulls Waste as Potential Adsorbent for Removal of Pb(II) and Ni (II) from Water, *Chemical Engineering Journal*, 197, 24–33
- Sarkar, M. and Majumder, P. (2011). Application of Response Surface Methodology for Optimization of Heavy Metal Biosorption Using Surfactant Modified Chitosan Bead *Chemical Engineering Journal*,175 (15): 376-387.
- Tsai, W.T. and Chen, H.R. (2010). Removal of Malachite Green from Aqueous Solution using Low-Cost Chlorella-Based Biomass. *Journal of Hazardous Materials*, 175: 844–849.
- Upatham, E.S., Boonya, B., Kriatracjie, M., Pokethitiyook, P. and Park, K. (2002). Bio-sorption of Cadmium and Chromium in Duck Weed *Wolffia globosa*. *International Journal of Phytol.*, 4(2), 73-86.
- Wang J. L. (2002). Immobilization Techniques for Biocatalysts and Water Pollution Control. Beijing: Science Press.

World Health Organization (2000). Environmental Lead Exposure: A Public Health Problem of Global dimensions. WHO Bulletin, Tong S, Yasmin E, Von S, Prapamontol T, (eds.) Geneva, Switzerland.