APPLICATION OF RESPONSE SURFACE METHODOLOGY IN ADSORPTION OF LEAD ION FROM LABORATORY SIMULATED WASTEWATER USING *Eucalyptus Tereticornis* LEAVES

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ABSTRACT
This study is aimed at modeling of lead adsorption on Eucalyptus tereticornis (locally known as Turare) leaves from laboratory simulated wastewater through the application of response surface methodology (RSM). Batch studies were performed to evaluate the different parameters considered: contact time and adsorbent dosage. Central Composite Design (CCD) in Response Surface Methodology was employed which gave a total of 13 experimental runs that lead to a quadratic model relating the response (adsorption capacity) and the variables. Analysis of variance (ANOVA) indicated that the model was significant as indicated in model P-value of 0.0001. Significant model terms were (contact time) and (adsorbent dosage). Experimental results showed that at constant pH 5, the adsorption capacity has reached a maximum of 0.8147 mg/g with a contact time of 70 min. Optimization of the model indicated adsorbent dosage of 1 g/L and 120 min adsorption time as optimum conditions for the process. The actual and predicted values of the response agreed closely as evidenced from the model R^2-Value of 0.9651.

Keywords: *RSM, lead (Pb), simulated wastewater, Eucalyptus tereticornis and model.*

1.0 INTRODUCTION

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Heavy metal ions such as cobalt, copper, nickel, chromium, lead, and zinc are detected in the waste streams from mining operations, tanneries, electronics, electroplating, batteries and petrochemical industries as well as textile mill products (Kadirvelu *et al*., 2001; Williams *et al*., 1998). Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders, therefore they must be removed before discharge.

Major lead pollution is through automobiles and battery manufacturers (Kobya *et al*., 2005). Lead is considered as one of the top sixteen toxic pollutants because of its carcinogenic characteristics for humans (Phussadee *et al*., 2008). The permissible limit of lead ion in drinking water is 0.05 mg/L. The maximum discharge limits for Pb ion in waste water is 0.05 mg/L and sewage sludge applied to agriculture land is 420 mg/L as set by the Environment protection Agency (Brady and ray, 1999). Lead poisoning causes severe damage to the kidneys, nervous system, reproductive system, liver and brain. Contamination of water through anthropogenic practices is the primary cause of lead poisoning in fish. The several methods which were used for the treatment of waste water include Precipitation, adsorption with activated carbon, ion exchange and membrane processes (Namasivayam and Ranganathan, 1995).

Adsorption is one of the physicochemical treatment processes found to be effective in removing heavy metals from aqueous solutions (Bailey *et al*., 1999). An adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a byproduct of waste material from waste industry. Studies have been carried out to ascertain the optimum conditions necessary for efficient removal of these metals from polluted sites.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables on the response. The RSM generates an experimental design for model preparation. An experimental design is a specific set of experiments defined by a matrix composed of the different level combinations of the variables studied (Junqueira *et al*., 2007).

In this study, RSM was employed in modeling and optimization of biosorbent developed from *Eucalyptus tereticornis* leaves which belongs to the family *Myrtaceae*, and used for the removal of Pb (II) ions from contaminated water. The factors studied were contact time and dosage.

2.0 MATERIALS AND METHODS

The leaves of *E. tereticornis* were collected from Ahmadu Bello University, Zaria. They were washed to remove the suspended particles and dried for some days to remove the moisture content. The sample was ground approximately to a particles size of 1.4mm of sieve size. The samples were kept in an air tight plastic jar until the usage for the experiment.

2.1 Preparation of adsorbent

Metal ion solution of Pb (II) was prepared from Lead nitrate (Merck- A.R. grade). About 1.598 g of lead nitrate was weighed and a standard stock solution of concentration 1000 mg/L was prepared in double distilled water. The initial and final concentrations of metal ions were analyzed by Atomic Adsorption

Spectrometry (AAS), model AAS500 manufactured by Jasco Equipment.

2.2 Design of experiment

A Central Composite Design (CCD) under Response Surface Methodology in Design Expert 6.0.6 version was employed (Zahedi and Azarpour, 2011; Galadima *et al*., 2015) and 13 experimental runs were obtained with two chosen factors. These factors were varied at two levels, low and high as presented in Table 1

TABLE 1: DESIGN SUMMARY

Factors	Name	Unit	Lower Limit	Upper Limit	Low coded	High coded
A	Contact time	Minutes	20.00	120.00	-1	1
B	Adsorbent dosage	Gram	1.000	5.000	-1	1

3.0 RESULTS AND DISCUSSIONS

Table 2 presents the central composite design matrix and the adsorption capacity obtained from the experimental runs. It can be seen from the Table that 0.0211 and 0.8147 were the lowest and highest adsorption capacity achieved respectively.

Table 2: CENTRAL COMPOSITE DESIGN OF THE EXPERIMENT WITH THE RESPONSE

Runs	Time (min)	Adsorbent Dosage (g/L)	Adsorption Capacity (mg/g)
1	20.00	1.00	0.1231
2	70.00	3.00	0.0564
3	70.00	3.00	0.0462
4	120.00	5.00	0.0246
5	70.00	5.83	0.0211
6	120.00	1.00	0.2308
7	20.00	5.00	0.0338
8	70.00	3.00	0.0756
9	140.71	3.00	0.0769
10	70.00	0.71	0.8147
11	70.00	3.00	0.0769
12	0.71	3.00	0.0821
13	70.00	3.00	0.0718

The results of the second order response surface model fitting in the form of Analysis of Variance (ANOVA) are given in Table 3. The ANOVA table indicated that the model was significant due to the model P-value of 0.0001. Significant model terms were B and B^2 also due to their P-value of <0.0001. The "Lack of Fit F-value" of 0.52 implies the Lack of Fit is not significant relative to the pure error. This implies that the model will fit data.

The value of the determination coefficient (R^2= 0.9651) indicates that 96.51% of the variability in the response could be explained by the model. In addition, the value of the adjusted determination coefficient R^2 (Adj) = 0.9401 is also very high to advocate for a high significance of the model. The predicted adsorption capacities resulted from the model were in close agreement with the experimental values also as evidenced from the R^2 values and hence the model was adequate in representing the adsorption capacity of lead under the specified conditions.

The final equation in terms of actual value is given as:

$$1/(Adsorption\ capacity) = 7.69617 - 0.028678(\mathrm{A}) - 2.03873(\mathrm{B}) - 4.40287 \times 10^{-4}(\mathrm{A}^2) + 1.18814(\mathrm{B}^2) + 0.037138(\mathrm{AB})$$

where: A and B represent contact time and adsorbent dosage respectively.

TABLE 3: ANOVA FOR INVERSE TRANSFORM SURFACE QUADRATIC MODEL TO IDENTIFY SIGNIFICANT CONTRIBUTING FACTORS

Source	Sum of square	DF	Mean square	F-value	Prob>F
Model	2135.75	5	427.15	38.66	< 0.0001
A	8.90	1	8.90	0.81	0.3992
B	1893.29	1	1893.29	171.35	*< 0.0001*
A2	8.43	1	8.43	0.76	0.4114
B2	157.39	1	157.39	14.24	0.0069
AB	55.17	1	55.17	4.99	0.0606
Residual	77.34	7	11.05		
Lack of fit	21.57	3	*7.19*	0.52	0.6934
Pure error	55.78	4	13.94		
Corr total	2213.09	12			

Adeq precision=20.221, R^2= 0.9651 and Adjusted R^2= 0.9401 significant variable (P>F<0.05)

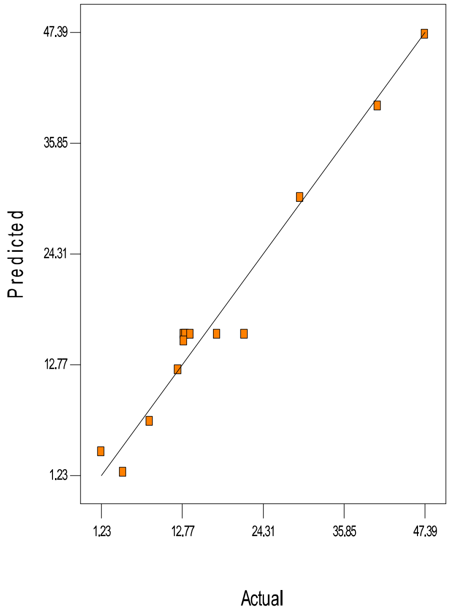

Figure 1: Parity plot of actual and predicted values for Pb adsorption capacity (AC) on *Eucalyptus tereticornis* Leaves

The parity plot (Figure 1) showed a satisfactory correlation ($R^2 = 0.9657$) between the experimental and the model predicted values of lead adsorption capacity. The points are on the diagonal line which indicated the good fit of the model due to the slight deviation between the experimental and predicted values of the response as seen from the value of the correlation coefficient.

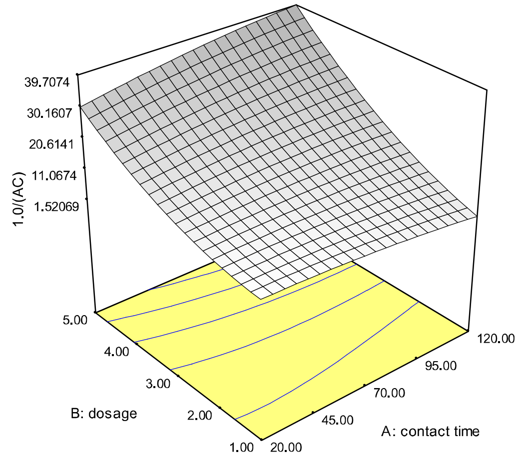

Fig 2: 3D response surface for inverse of adsorption capacity versus the effect of contact time and adsorbent dosage.

Figure 2 presents the variation of contact time and adsorbent dosage with inverse adsorption capacity of lead. It can be seen from the Figure that the lower the inverse of the response the higher the adsorption, also lower dosage values indicated relatively higher adsorption while time variation does not significantly affect the response.

Tables 4 and 5 present the constraints and the optimization results respectively. The goal is to maximize the adsorption capacity. The results indicated that 0.6576 is the optimum capacity at 120 min and adsorbent dosage of 1 g/L. This is the result with the highest desirability of 0.994 (99.4 %).

TABLE 4: CONSTRAINTS OF OPTIMIZATION PARAMETERS OF LEAD ADSORPTION ON *E.Tereticornis* LEAVES

Name	Goal	Lower Limit	Upper Limit
Contact time (min)	Is in range	20.00	120.00
Adsorbent dosage (g)	Is in range	1.000	5.000
Adsorption capacity (mg/g)	Maximize	0.0211	0.8147

TABLE 5: RESULTS OF THE OPTIMIZATION OF LEAD ADSORPTION ON *E.Tereticornis* LEAVES

S/N	Time, min	Dosage, g/L	Adsorption Capacity, mg/g	Desirability
1	120	1.0	0.6576	0.994
2	120	1.37	0.2973	0.954
3	42.23	1.0	0.1558	0.888
4	34.87	1.0	0.1514	0.884
5	25.77	1.0	0.1477	0.880

4.0 CONCLUSIONS

Adsorbent developed from *Eucalyptus tereticornis* leaves was successfully employed for lead adsorption from wastewater. The process was modeled and optimized; and analysis of variance (ANOVA) indicated that the model was significant (p-value of 0.0001). Adsorbent dosage was also found to be a significant model parameter. Optimization of the adsorption process revealed that the optimum contact time and the adsorbent dosage were 120 min and 1.0 g/L respectively; this resulted in 0.6576 mg/g adsorption capacity.

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