[1.] S.E. UWADIAE, [2.] O.M. EDOKPIAWE

MODELLING AND OPTIMIZATION OF LEAD ADSORPTION FROM AQUEOUS SOLUTION USING GROUNDNUT SHELL

[1,2] Department of Chemical Engineering, Faculty of Engineering, University of Benin, Benin City, Edo State, NIGERIA

Abstract: In this study, the design of experiment for response surface methodology (RSM) was used to analyse and optimise the simultaneous effect of adsorbent dose, contact time and pH of solution during the removal of Pb(II) ion from aqueous solution using activated carbon developed from groundnut shell as adsorbent. Groundnut shells were collected from a dust bins and thoroughly washed with distilled water; sun-dried and pulverized. It was thereafter carbonated using a muffle furnace at 500°C for 1 hour, after which the carbonated groundnut shell was sieved to attain 0.425mm or less before activation using nitric acid. A three-variable and three-level Box-Behnken factorial design was used to develop a statistical model to describe the relationship between percentage removal of Pb^{2+} and the selected independent variables. The selected parameters were then optimised using RSM. The model was statistically significant ($p<0.0001$) with a low standard deviation of 0.76 and did not show lack of fit ($R^2=0.9768$). The optimum values of adsorbent dose, contact time and pH of the solution obtained from RSM were 0.94 g, 5115.36 min and 5.42 respectively. The observed results indicate the viability of activated carbon from groundnut shell for removal of Pb^{2+} from aqueous solution and industrial wastewater.
Keywords: Groundnut-shell, activation, Box-Behnken design, Response surface methodology, Optimization

INTRODUCTION

Because of advancement and industrialization in numerous nations, the levels of modern contamination have been relentlessly rising. Thusly, the treatment of dirtied mechanical wastewater remains a point of worldwide worry since wastewater gathered from regions, groups, and enterprises should, at last, come back to getting water or to the land. In addition, sullying of groundwater is today a noteworthy worry in the administration of water assets (Weber, 1991). Natural contamination because of the release of substantial metals from different businesses, including metal plating, mining, painting and horticultural sources, for example, manures and fungicidal showers are of noteworthy concern in view of their danger and risk to human life, particularly when resilience levels are surpassed (Gupta *et al.*, 2009). Various treatment techniques for the expulsion of metal particles from fluid arrangements have been accounted for. This incorporates diminishment, particle trade, electrodialysis, electrochemical precipitation, dissipation, solvent extraction, reverse osmosis, substance precipitation and adsorption (Gupta *et al.*, 2009). Adsorption processes are not sophisticated and also not complicated hence it has found wide usage for treatment of wastewater (Mabrouk *et al.,* 2009). Since it is highly efficient, commercial activated carbon (CAC) is a commonly used adsorbent in the adsorption process for the treatment of wastewater but it is however expensive (Aksu, 2005).

Because of the high cost of CAC and misfortune amid recovery, alternative low-cost adsorbents have pulled in the consideration of a few researchers to give a contrasting option to the costly CAC. The low-cost adsorbents include banana and orange peels (Annadurai and Lee, 2002); Sheep Hoofs (Touaibia and Benayada, 2006); *Luffa Cylindrica* (Oboh *et al.*, 2011) and sawdust (Šćiban *et al.*, 2006).

Regular and classical techniques for concentrate a procedure by keeping up different elements required at determined steady levels don't delineate the consolidated impact of the considerable number of components included. This strategy is likewise tedious and requires various tests to decide ideal levels (Chaisongkroh *et al.,* 2012). Apart from being a tool that is employed to optimize and study interactions among factors, response surface methodology (RSM) likewise the relative importance of different variables engaged with complex collaborations can be assessed (Saha *et al.*, 2009). The general objective of the study was to investigate the effectiveness of activated carbon formulated from locally available groundnut shell for the removal of lead ions from aqueous solution.

MATERIALS AND METHODS

— Preparation of Activated Carbon

The groundnut shells were collected from a dustbin in a local market in Benin City, Nigeria. They were then thoroughly washed with distilled water so as to remove all adhering particles before sun-drying for 5 days. The dried samples were pulverized and weighed on a digital weighing balance. The measured groundnut shell was placed in the muffle furnace at 500°C for 1 hour, after which the carbonated groundnut shell was sieved to attain 0.425 mm or less before activation. The activation was done by soaking the sieved carbonated groundnut shell in the solution of nitric acid, at a ratio of 1:4 by mass of groundnut shell to nitric acid, for 24 hours for activation purposes. Then the activated groundnut shells were removed from the solution and placed in the oven for 2 hours, at 60°C; it was then left to cool in a desiccator. After cooling, the groundnut shell was washed with distilled water and placed in a container, and dried in the oven for another 4.5 hours, at 105°C.

— Preparation of Aqueous Solution

Stock solution of Pb (II) ion was prepared by dissolving analytical grade $Pb(NO_3)_2$ in an appropriate amount of distilled water. From this stock solution a working solution of 100 mg/L of Pb (II) ion was prepared which was used for the batch adsorption process.

— Adsorption Experiment

Batch adsorption experiments were carried out for the removal of Pb^{2+} from aqueous solutions onto the adsorbent to study the effect of some specific process parameters. The effects of adsorbent dosage, contact time and pH were investigated for the adsorption onto groundnut shell. 100mg/l of concentration of lead(II) ions was used as the working solution. The adsorption was carried out at ambient temperature and shaking speed of 250 rpm in an orbital shaker. After filtrations, the residual concentrations of Pb(II) were determined using atomic adsorption spectrophotometer (AAS).

The percentage removal of Pb^{2+} is defined as:

$$\mathrm{Re}\ \% = \frac{Ci - Cf}{Ci} \times 100 \quad (1)$$

where: Re (%) is percentage removal of Pb(II) ions, C_i is the concentration of Pb(II) ions before adsorption (mg/l); C_f is the concentration of Pb(II) ions after adsorption (mg/l)

— Experimental Design

A 3-stage-three-element Box-Behnken factorial layout was accomplished using design Expert, version 7.1.6 (Stat-Ease Inc., Minneapolis, MN, USA) to determine the best combination of adsorption variables for the yields of Pb(II) ions.

The variable input parameters were pH of the solution, contact time and adsorbent. As shown in Table 1, independent variables had three levels which were based on preliminary experiments.

Table 1: Independent variables and their levels for BBD experimental design

Independent Variable	Symbols	Coded and Actual Levels		
		-1	0	1
Adsorbent dose (g)	X_1	0.2	0.6	1
Contact time (min)	X_2	10	65	120
Ph	X_3	2	4	6

The response was percentage removal of Pb(II) ions. The relation between the coded values and actual values are described as follows:

$$x_i = \frac{X_i - X_0}{\Delta X} \quad (2)$$

where x_i and X_i are the coded and actual values of the independent variable respectively. X_o is the actual value of the independent variable at the centre point and ΔX_i is the step change in the actual value of the independent variable. The following generalized second order polynomial equation was used to estimate the response of the dependent variables.

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} {X_i}^2 + \sum\sum b_{ij} X_i X_j + E \quad (3)$$

where Y_i is the predicted response, X_i and X_j are the independent variables, b_o is offset term, b_i and b_{ij} are the single and interaction effect coefficients and E is the error term. Based on RSM, this equation was used to evaluate the linear, quadratic and interactive effects of independent variables on the chosen response. For the model, the calculations from the linear and cross regression were performed. The R^2 value, the residual error, the pure error calculated from the repeated measurements and the lack of fit were calculated. ANOVA was utilized to estimate the measurable attributes of the model fitting. The total test outline and results comprising of coded levels, real factors, and responses are given in Table 2. Keeping in mind the end goal to guarantee a good model, a test for criticalness of the relapse model and individual model coefficients was performed together with the absence of-fit test. Regularly, the huge components can be positioned in light of the F-value or p-value. The bigger the extent of the F-value and correspondingly the smaller the p-esteem, the more critical is the comparing coefficient (Yi *et al.*, 2010).

RESULTS AND DISCUSSION

The complete experimental design and results consisting of coded levels, actual variables, predicted and experimental responses are given in Table 2.

Table 2: Box Behnken design matrix for the optimization of variables and the response values

Run No.	Factors						Response Percentage Pb(II) ion removal	
	Coded values			Actual values				
	x_1	x_2	x_3	X_1	X_2	X_3	Experimental	Predicted
1	0	0	0	0.6	65	4	90	91.66
2	0	1	1	0.6	120	6	99.1	99.11
3	-1	-1	0	0.2	10	4	98	98.02
4	0	-1	1	0.6	10	6	98.8	98.88
5	1	-1	0	1	10	4	96.65	96.55
6	0	0	0	0.6	65	4	91.5	91.66
7	0	0	0	0.6	65	4	92	91.66
8	0	0	0	0.6	65	4	92.5	91.66
9	0	-1	-1	0.6	10	2	97.75	97.74
10	1	0	1	1	65	6	99.8	99.82
11	1	0	-1	1	65	2	98.4	98.5
12	1	1	0	1	120	4	99.02	98.996
13	0	0	0	0.6	65	4	92.3	91.66
14	-1	1	0	0.2	120	4	96.79	96.89
15	-1	0	1	0.2	65	6	99	98.9
16	-1	0	-1	0.2	65	2	98.8	98.78
17	0	1	-1	0.6	120	2	98.9	98.82

As appeared in Table 2, the entire plan comprised of 17 trial focuses, and five duplicates (run 13– 17) at the focal point of the outline were utilized for evaluating the trial blunder entirety of squares.

Investigation of fluctuation (ANOVA) is a measurable strategy that subdivides the aggregate variety in an arrangement of information into segment parts related with particular wellsprings of variety to test speculations on the parameters of the model (Francesc and Julia, 2014).The results of the analysis of variance (ANOVA) which are given in Table 3.

Table 3: ANOVA table for quadratic model

Sources	Sum of squares	Degree of freedom	Mean square	F value	P value prob>F
Model	171.11	9	19.01	32.73	<0.0001
X_1	0.2	1	0.2	0.35	0.5714
X_2	0.85	1	0.85	1.47	0.2653
X_3	1.02	1	1.02	1.75	0.2277
X_1X_2	3.2	1	3.2	5.52	0.0512
X_1X_3	0.36	1	0.36	0.62	0.457
X_2X_3	0.18	1	0.18	0.31	0.5945
X_1^2	42.01	1	42.01	72.32	<0.0001
X_2^2	32.92	1	32.92	56.67	0.0001
X_3^2	73.61	1	73.61	126.71	<0.0001
Residual	4.07	7	0.58		
Lack of fit	0.0055	3	0.018	0.018	0.9961
Pure Error	4.01	4	1		
Cor Total	175.18	16			
Std dev	0.76		R^2		0.9768
Mean	96.43		Adjusted R^2		0.9469
C.V (%)	0.79		Predicted R^2		0.9592
PRESS	7.14		Adequate precision		13.952

ANOVA table proposes whether the condition is sufficient to depict the connection amongst reaction and other autonomous factors. The model can be considered as factually noteworthy, if the estimation of p is lower than 0.05 with a bigger F-value (Ravikumar *et al.*, 2013. From the ANOVA table it is observed that the model fitted well with the information created and can be considered as factually noteworthy since the F-value is large. (32.73) and p value is lesser than 0.0001. The goodness of the model was assessed through the lack of fit test. The P-values for the lack of fit test was not significant ($p>0.05$) demonstrating that the model was fit for predicting the adsorption of Pb(II) ions onto activated carbon planned from groundnut shell. A good fit means that the generated models adequately explained the data variation.

An R^2 value of 0.9768 means that 97.68 % of the variations for percent lead ion adsorption are explained by the independent variables and this also means that model does not explain only 2.32 % of the variation. Predicted R^2 is a measure of how good the model predicts a response value.

The predicted R^2 value of 0.9592 is in reasonable agreement with an adjusted R^2 value of 0.9469. The coefficient of variation, C.V. obtained was 0.79 %. . C.V is an indication of the degree of precision with which the treatments were carried out. A low value of C.V suggests a high reliability of the experiment (Montgomery, 2005; Mason *et al.,* 1989). "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable (Cao *et al.,* 2009), therefore the ratio of 13.952 indicates an adequate signal

Design Expert software was used to calculate the coefficients of the second-order fitting equation and the model suitability was tested using the ANOVA test. Therefore, the second order polynomial equation should be expressed by Eq. (4`)

$$Re = 120.04394 - 27.43494X_1 - 0.13092X_2 - 8.28381X_3 + 0.040682X_1X_2 + 0.37500X_1X_3 - 1.93182X10^{-3}X_2X_3 + 19.7421{X_1}^1 + 9.24380X10^{-4}{X_2}^2 + 1.04531{X_3}^2 \quad (4.)$$

According to the monomial coefficient value of regression model Eq. (4), X_1 = ´-27.4349; X_2= ´-0.13092 and X_3 = -8.28381 (pH), and the order of priority among the main effect of impact factors is $X_1 > X_3 > X_2$

The created information was examined to decide the connection between's the genuine and anticipated esteems as appeared in Figure 1.

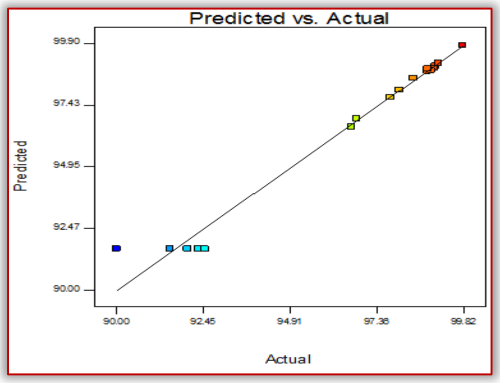

Figure 1: Plot of predicted against actual lead ion percentage removal.

From Figure 1 it is watched that the information focuses are conveyed close to the straight line showing that the quadratic model could be utilized as the noteworthy model for anticipating lead (II) ions removal over the autonomous information factors.

The effects of contact time and adsorbent dose, pH of solution and contact time, and pH of the solution and adsorbent dose on Pb(II) ions percentage are shown in the response surface plots presented in Figures 2- 4.

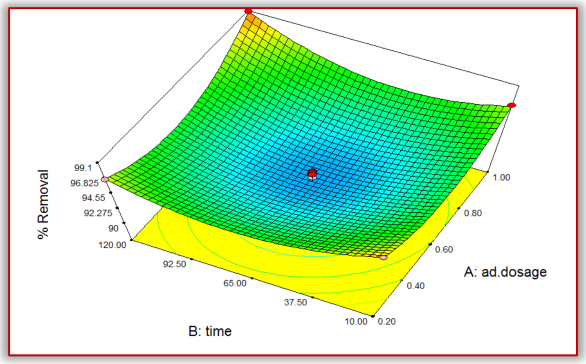

Figure 2: Response surface plots showing the effect of adsorbent dosage and time on Pb(II) ion removal

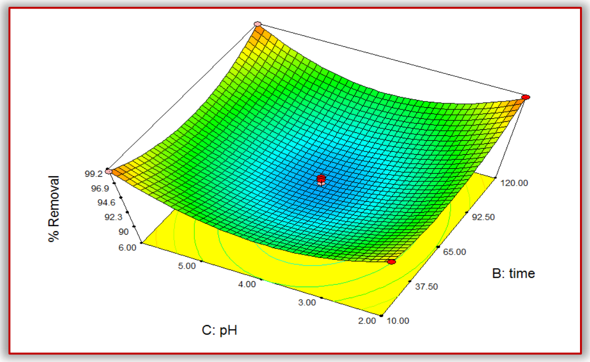

Figure 3: Response surface plots showing the effect of time and solution pH on Pb(II) ion removal

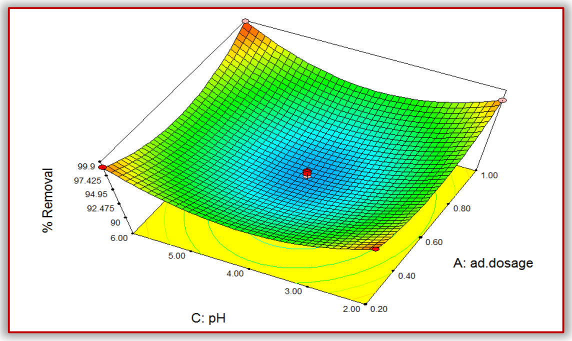

Figure 4: Response surface plots showing the effect of adsorbent dosage and pH of the solution on Pb(II) ion removal

The association between contact time and adsorbent dosage and the cooperation between contact time and pH had a general beneficial outcome on removal the of Pb(II) from the aqueous solution; as contact time and the adsorbent dose increased, removal of Pb(II) ion likewise increased. A comparative pattern was noticed when contact time and pH increased. Be that as it may, as both adsorbent measurement and pH increased, the removal of Pb(II) from aqueous solution diminished.

Following the optimization step, corresponding optimum conditions for optimum values of Pb(II) ion removal were obtained thus; adsorbent dosage (0.94 g), contact time (115.36 min), and pH (5.42).

CONCLUSION

The production of activated carbon from groundnut shell which is an agricultural waste/by-product is a value addition to the groundnut residue. The formulated activated carbon from groundnut shell was used in the removal of Pb(II) ion from aqueous solution. The effects of adsorbent dose, contact time and pH of the solution on the sorption of Pb(II) onto the activated carbon was investigated, Furthermore, statistical methodology, employing Box-Behnken Response Surface Design was used to determine the optimal conditions for the adsorption of Pb(II) ion onto the developed activated carbon from groundnut shell. The optimal conditions for Pb(II) ion removal from aqueous solution is identified as adsorbent dose of 0.94 g, contact time of 115.36 min and pH value of 5.42. It can be concluded that groundnut shell can serve as ready raw material for the development of affordable and effective activated carbon which can serve as a good adsorbent for the removal of Pb(II) ion from wastewater.

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