Optimization and Characterization of Adsorptive Behavior of Pentaclethra Macrophylla Activated Carbon on Aqueous Solution

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***Abstract*– Biosorption potentials of activated carbons from pentaclethra Macrophylla (PMAC) seed shells for the removal of Pb(II) from aqueous solution were investigated. The physicochemical properties of pentaclethra Macrophylla (PMAC) seed shells were characterized through ASTM standards for adsorbents tests. The functional groups of the pentaclethra Macrophylla (PMAC) were investigated using Fourier transform infrared (FTIR) spectroscopy, morphology measured with scanning electron microscopy (SEM), oxides investigated by X-ray fluorescence (XRF) and diffraction pattern observed by x-ray diffraction (XRD). Influence of key parameters such as contact time, pH of pb(II) solution, temperature of Pb(II) solution, adsorbent dosage, adsorbent particle size and initial concentration of Pb(II) solution were studied by batch mode. These process parameters were optimized using response surface methodology (RSM) and analysis of variance (ANOVA). The significance of the different process parameters and their combined effects on the adsorption efficiency were established through a full factorial central composite design. The results obtained are in good agreement with published data for other activated carbons as well as various international standards for water treatment. An optimal yield of 94.83% was obtained with optimal conditions of solution temperature, 30^0C; contact time, 120minutes; adsorbent dosage, 1.50 g; and pH, 7. The optimization was performed using the numerical method of the Design Expert version 8.7.1.0 by State Ease U.S.A. This investigation has shown that pentaclethra Macrophylla (PMAC) seed shells from Nigeria can be used for industries as activated carbon for waste water treatment.**

***Keywords*– Adsorption, Optimization, Pentaclethra Macrophylla (PMAC), Seed Shells and Response Surface Modeling**

I. INTRODUCTION

In recent years contamination of the environment from a variety of sources has become an increasingly serious problem. Rapid industrialization has led to increased disposal of heavy metals into the environment. Heavy metals such as lead, copper, cadmium, zinc and nickel are among the most common pollutants found in industrial effluents. These metals, if present beyond certain concentration can be toxic to organisms, including humans can be toxic to organisms, including humans [I], [2]. Heavy metals cannot be degraded or rapidly detoxified biologically [3]. Lead is the one of the most toxic pollutant which cause severe environmental and health problems. The major source of lead pollution in wastewaters is discharging of waste stream from acid battery manufacturing, pigments, metals plating and finishing, printing, lead mining, metallurgical alloying, gasoline additives, ceramics and glass industries [4], [5], [6]. The presence of lead in drinking water even at low concentration may cause such diseases as anemia, encephalopathy, hepatitis and nephritic syndrome [6]. Excess intake of lead by humans causes disruption in the biosynthesis of the hemoglobin level, a rise in blood pressure, kidney damage, miscarriages and abortions, brain damage, and diminished learning abilities in children. Furthermore, lead is a known carcinogen [2]. These lead containing effluents, therefore, must be adequately treated prior to discharge into receiving water bodies to ensure good human health and environmental quality [5], [7].

Several physico-chemical treatments have been used for removing heavy metals such as ions exchange, chemical precipitation, coagulation/flocculation, membrane filtration, solvent extraction, sedimentation, biological operations, electrochemical processes and adsorption. Most of these processes are costly and lead to generation of sludge or formation of by-products [8], [9]. Among all the techniques adsorption is more popular due to low operating cost, specific selectivity of the metals and no production of secondary toxic compounds [10]. Many non conventional adsorbents, such as agricultural and industrial solid wastes like activated carbon prepared from Moringa Oleifera, waste fruit cortex, red algae, coconut husk, tea leaves, cocoa shells, orange peel, maize cob, olive cake and soyabean hull [7] have been studied. Low cost adsorbents for wastewater treatment have shown great prospects as adsorbents due to their renewability, natural abundance, low cost and eco-friendly [11], [12].

Pentaclethra macrophylla (PM), is a multiusage tree from Africa and belongs to the leguminous family; sub-family of mimosoideae found mostly in tropical Africa. It has been cultivated in Nigeria since 1937. The tree grows to about 21m in height and about 6 m in girth. PM seeds are eaten in the form of salad across different African countries [13]. It is used as food, salt substitute, edible oil, seed craft, dye, fencing and palings, charcoal, carving bowls, medicine for convulsion, itching, lactogenicity and ornamental [14].

In this study, response surface methodology in combination with central composite design was applied to optimize and

evaluate interactive effects of adsorption independent variables. The response surface methodology (RSM) is being proposed to determine the influences of individual factors and their interactive effects in the search of the optimum conditions for desirable responses. By these, the interactions of possible parameters that influence adsorption on treatment efficiency could be evaluated with a limited number of planned experiments using the RSM. A central composite design (CCD) was employed for this optimization usage of the response surface methodology (RSM).

II. MATERIALS AND METHODS

A) Materials

Pentaclethra macrophylla (PM) seed shells were collected from oil bean sellers at Eke Awka market in Anambra, reagents and $Pb(NO_3)_2$ salt were obtained from Head Bridge Onitsha in Anambra State, Nigeria.

B) Methods

De-ionized water of pH 7.0 was used to wash the seed shells to remove dirt and other surface adhere particles, and then dried at 110^0C for 12hours to obtain a constant weight. Dried PM seed shells were ground and sieved to 1- 3.0mm particle size and stored for further use. The dried PM seeds shells were soaked in 60% H_3PO_4 at room temperature for 24 hours and carbonized at 773K for 90 minutes using muffle furnace with identification model number SX-2.5-10. De-ionized water of pH 7 was used to wash the carbonized samples in order to neutralize the acidic content present in the adsorbent until it reached the pH of 7, drained and dried in an oven at temperature 378K for 240minutes. The activated carbon (PMAC) produced was kept in a desiccator for cooling to room temperature, sieved to different adsorbent particle sizes and finally kept in an air tight container for the adsorption study.

A stock solution of 1000mg/L Pb(II) was prepared from $Pb(NO_3)_2$ salt. 0.1g of the lead was dissolved with de-ionized water in 1000ml (1 litre) get a lead solution of 100mg/L. Other concentrations of Pb(II) solution used in the experiments were prepared by appropriate dilution of the stock solutions. The experiments were performed by putting a known dose of adsorbents to100 ml stock solution of lead at stirring speed of 120rev/min for the treatment. After some time of treatment, the Pb(II) solution was filtered and the concentration of the residue was tested using Atomic Absorption Spectrophotometer with identification model number of AA 220FS. The amount of Pb(II) uptake per unit mass of activated carbon (mg/g) and percentage removed (%) were determined with equation 1 and equation 2:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$\text{Percentage adsorded} = \frac{Co - Ce}{Co} \times 100 \quad (2)$$

Where, C_0 and C_e is the Pb(II) initial and final concentration in the solution (mg/L); W is the weight of activated carbon (g) and V is the volume of the Pb(II) solution (L).

C) Pysiochemical characterization of the activated carbon

The physicochemical properties of Pentaclethra macrophylla activated carbon (PMAC) was determined using methods described by [15].

D) Instrumental Characterization

The surface functional groups on PMAC were identified using FTIR spectrophotometer with model number Shimadzu FTIR 8400, the surface morphology of the activated carbon (PMAC) was examined with SEM microscopy with identification number Phenom Prox, XRD diffractometer with model number Stchmabzu model 6000 was used to observe the diffraction pattern and inter planar spacing of PMAC with Cuk_α radiation having a scanning speed of 8000deg/min and examined at 40kV and 30mA. XRF spectrometer with model number municipal 4 was used to examine the chemical groups and oxides present in the activated carbon (PMAC).

E) Design of Experiment

Design Expert software (version 8.0.7.1) was used in this study to design the experiment and to optimize the reaction conditions. The experimental design employed in this work was a central composite design (CCD) a two-level-four-factor ($2^4 + 2 * 4 + 6$), including 30 experiments. Temperature, A, contact time, B, adsorbent dosage, C, solution pH, D were selected as independent factors for the optimization study. The response chosen was the Adsorption efficiency obtained from the adsorption Pb(II) on Pentaclethra macrophylla activated carbon (adsorbent) . The coded values of the process variables were determined using equation 3:

$$x_i = \frac{X_i - X_0}{\Delta x} \quad (3)$$

Where x_i –coded value of I^{th} variable, X_i- un-coded value of the I^{th} test variable and X_0 - un-coded value of the I^{th} test variable at center point.

The factors levels with the corresponding real values and the design matrix are shown in Table 1. The matrix for the four variables was varied at five levels (-α, -1, 0, +1, and +α). As usual, the experiments were performed in random order to avoid systematic error. The regression analysis was performed to estimate the response function as a second-order polynomial using Equation 4:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1,i<j}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \quad (4)$$

Where Y is the predicted response, β_i, β_{ii}, β_{ij} are coefficients estimated from regression. They represent the linear, quadratic and interactions of the independent variables on the response. Selection of levels for each factor was based on the experiments performed to study the effects of process variables on the application of activated carbon for adsorption of Pb(II) as shown in Table 2.

Table 1: Independent variables and levels used for response surface design

Independent variable	Symbol	Range and Levels				
		-α	-1	0	+1	+α
Temperature (^{0}C)	A	20	30	40	50	60
Contact time (min)	B	30	60	90	120	150
Dosage (g)	C	0.38	0.75	1.13	1.50	1.88
Solution pH	D	2.5	4.00	5.5	7.0	8.50

Table 2: Experimental set up for 2-level-4-factor response surface design and the experimental and predicted values for Pb(II) removal by PMAC

Run No.	Temperature, ^{0}C (A)		Contact Time, min (B)		Adsorbent dosage g/l (C)		pH (D)		Adsorption Efficiency (%)	
	Coded values	Real values	Coded values	Real values	Coded values	Real values	Coded values	Real values	Experimental values	Predicted values
1	-1	30	-1	60	-1	0.75	-1	4	80.20	80.57
2	+1	50	-1	60	-1	0.75	-1	4	86.10	87.07
3	-1	30	+1	120	-1	0.75	-1	4	83.01	83.13
4	+1	50	+1	120	-1	0.75	-1	4	87.40	85.85
5	-1	30	-1	60	+1	1.50	-1	4	78.00	79.45
6	+1	50	-1	60	+1	1.50	-1	4	88.50	88.13
7	-1	30	+1	120	+1	1.50	-1	4	86.10	86.03
8	+1	50	+1	120	+1	1.50	-1	4	90.40	90.93
9	-1	30	-1	60	-1	0.75	+1	7	76.00	75.92
10	+1	50	-1	60	-1	0.75	+1	7	86.10	86.10
11	-1	30	+1	120	-1	0.75	+1	7	79.30	79.60
12	+1	50	+1	120	-1	0.75	+1	7	87.01	86.01
13	-1	30	-1	60	+1	1.50	+1	7	76.30	77.78
14	+1	50	-1	60	+1	1.50	+1	7	89.80	90.13
15	-1	30	+1	120	+1	1.50	+1	7	86.00	85.48
16	+1	50	+1	120	+1	1.50	+1	7	94.50	94.06
17	-α	20	0	90	0	1.13	0	5.5	77.20	75.87
18	+α	60	0	90	0	1.13	0	5.5	90.00	90.95
19	0	40	-α	30	0	1.13	0	5.5	77.20	75.32
20	0	40	+α	150	0	1.13	0	5.5	80.30	81.80
21	0	40	0	90	-α	0.38	0	5.5	82.29	82.91
22	0	40	0	90	+α	1.88	0	5.5	90.85	89.85
23	0	40	0	90	0	1.13	-α	2.5	92.00	91.47
24	0	40	0	90	0	1.13	+α	8.5	89.80	89.95
25	0	40	0	90	0	1.13	0	5.5	92.00	93.50
26	0	40	0	90	0	1.13	0	5.5	93.00	93.50
27	0	40	0	90	0	1.13	0	5.5	94.00	93.50
28	0	40	0	90	0	1.13	0	5.5	94.00	93.50
29	0	40	0	90	0	1.13	0	5.5	94.00	93.50
30	0	40	0	90	0	1.13	0	5.5	94.00	93.50

III. RESULTS AND DISCUSSION

A) Characterization Results

Physicochemical characteristics of the activated carbon, the results of the physiochemical characteristics of the adsorbent are presented in Table 3. Physicochemical properties describe the suitability of an adsorbent for an adsorption process. The major characteristics (surface area, total pore volume, iodine number, moisture content) are in good agreement with the standard. From Table 3, it was that surface area, total pore volume, iodine number, moisture content, bulk density and ash content of the PMAC were 954.56 m^2/g, 2.42, 764.53 mg/g, 3.63%, 0.43 g/cm^2 and 5.87% for Pentaclethra Macrophylla acid activated carbon (PMAC). The high surface area and pore volume and volatile matter content decreased of the adsorbent were due to the activation process used which involved H_3PO_4. This was due to the pyrolytic effect where most of the organic substances have been degraded and discharged as gas and liquid tars leaving a material with high carbon purity [16].

Table 3: Physical Properties of the Activated carbon

Parameter/Adsorbents	PMAC
Ash content (%)	5.87
Surface area (m^2/g)	954.56
Bulk density (g/cm^2)	0.43
Total pore volume	2.42
Iodine number (mg/g)	764.53
Moisture content (%)	3.63

B) Instrumental characteristics of the activated carbon

FTIR Spectra

The FTIR spectra of activated carbon were carried out. Fig. 1 shows the FTIR spectrum pattern of PMAC which indicates a number of absorption peaks reflecting the complex properties of the adsorbents. Adsorption in the IR region takes place because of rotational and vibrational movements of the molecular groups and chemical band of a molecule [17]. FTIR analysis of carbon was done to predict the functional groups of the activated carbons from PMAC for the adsorption process. The peaks at 3926, 3797 and 3628 cm^{-1} are attached to O-H stretch in phenol and alcohols. The peaks at 3410 and 3235 cm^{-1} corresponded to the bonded –OH groups, while those around 3012 and 2902 cm^{-1} were assigned to C=H stretch in alkenes and C-H stretch in alkanes respectively. The peaks at 2677, 2566 and 2428 cm^{-1} were assigned to O-H stretch in carboxylic acids. The bands at 1985 and 1874 cm^{-1} were attributed to the aromatic combination while the peaks at 1607 and 1433 cm^{-1} were assigned to N-H blend in amines and O-H blend in carboxylic acids. Other significant band positions of PMAC are noted at 2780 cm^{-1} (indicative of methylamino, N-CH_3, C-H stretch), 2262 cm^{-1} (suggestive of aliphatic cyanide / nitrile), 2085 cm^{-1} (associated with transition metal carbonyl), 1316 and 1101 cm^{-1} (representing C-C stretch skeletal vibrations), 768 cm^{-1} (due to C-H bend [mono] in aromatics), 928 cm^{-1} (representing cyclohexane ring vibrations).

SEM Micrograph

Fig. 2 shows the Scanning Electron Micrograph (SEM) of PMAC. The micrograph seems to be rough with sponge-like protrusions quite prevalent in activated carbon. High level of porosity was observed on the PMAC showing that the activated carbon is very porous.

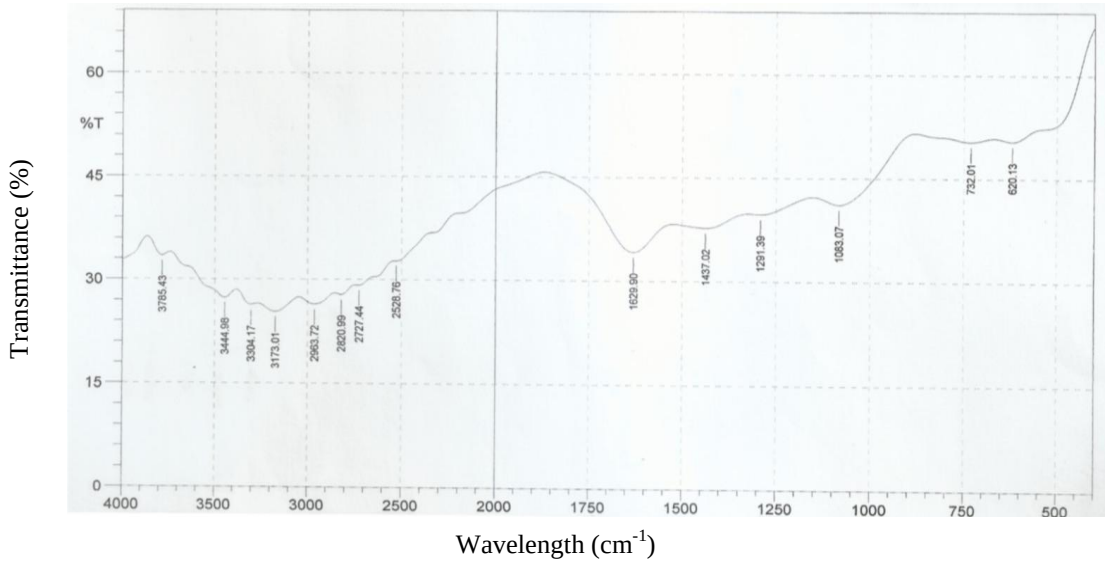

Fig. 1. FTIR spectra for the activated carbon (PMAC)

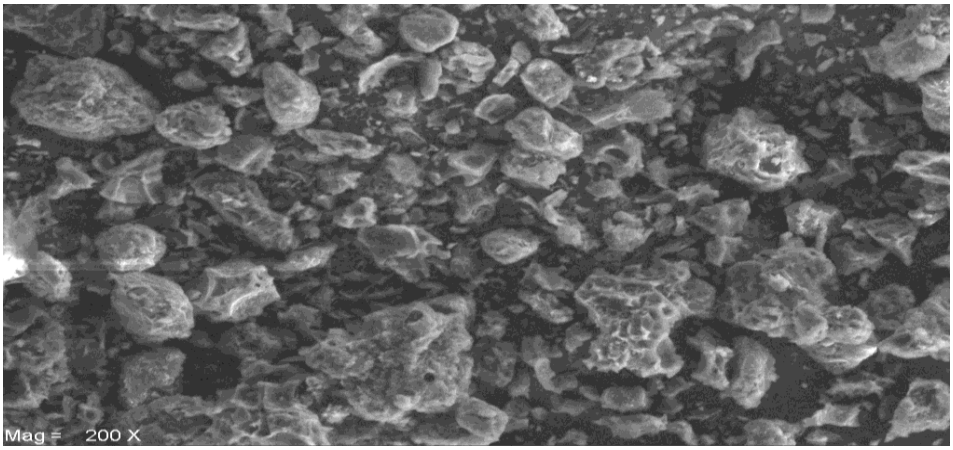

Fig. 2: SEM micrograph of PMAC

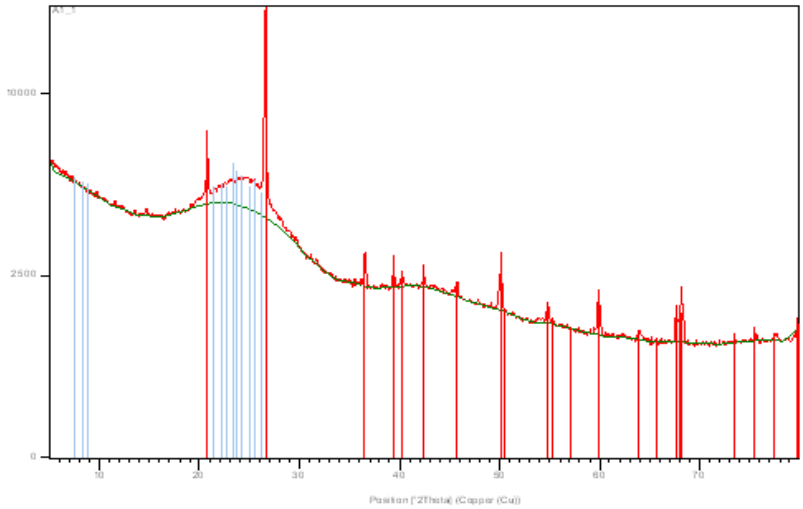

Fig. 3: XRD of the activated carbon

XRD Spectra

Fig. 3 shows the X-ray diffraction (XRD) profiles of PMAC. The XRD spectrum of the activated carbon as shown indicates the broad peaks. These broad peaks indicate the presence of high content of amorphous form of carbon and little amounts of crystalline materials in the adsorbent.

Evaluation of regression model for Pb(II) adsorption efficiency

The correlation between the experimental process variables and the adsorption efficiency was evaluated using the CCD modeling technique. Second order polynomial regression equation was fitted between the response (adsorption efficiency, (Y)) and the process variables: temperature (A), contact time (B), adsorbent dosage (C), and solution pH (D). From Table 4, the ANOVA results showed that the quadratic model is suitable to analyze the experimental data. The model in terms of the coded values of the process parameters is given by:

$$Y = 93.50 + 3.77\ A + 1.62\ B + 1.73\ C - 0.37D - 0.94\ AB + 0.54\ AC + 0.92\ AD + 1.00\ BC + 0.28\ BD + 0.74CD - 2.52A^2 - 3.735\ B^2 - 1.78\ C^2 - 0.70D^2 \quad (5)$$

To develop a statistically significant regression model, the significance of the regression coefficients was evaluated based on the p-values. The coefficient terms with p-values more than 0.05 are insignificant and are removed from the regression model. The analysis in Table 4 shows that all the linear terms save solution pH; all the quadratic terms, and the interaction terms of temperature and contact time; temperature and solution pH; contact time and adsorbent dosage and adsorbent dosage; are significant model terms. The model reduces to equation 8 after eliminating the insignificant coefficients.

$$Y = 93.50 + 3.77A + 1.62B + 1.73C - 0.94\ AB + 0.92\ AD + 1.00BC + 0.74CD - 2.52A^2 - 3.735B^2 - 1.78C^2 - 0.70D^2 \quad (6)$$

The analysis of variance indicated that the quadratic polynomial model was significant and adequate to represent the actual relationship between adsorption efficiency and the significant model variables as depicted by very small p-value (<0.0001). The significance and adequacy of the established model was further elaborated by high value of coefficient of determination (R^2) value of 0.9783 and adj. R^2 value of 0.9580. This means that the model explains 97.83% of the variation in the experimental data. The adequate correlation between the experimental values of the independent variable and predicted values further showed the adequacy of the model as illustrated in Fig. 4.

Response Surface Estimation

The interactive effects of the process variables on the percent metal ions removal efficiency were studied by plotting three dimensional surface curves against any two independent variables, while keeping other variables at their central (0) level. The 3D curves of the response (adsorption efficiency) from the interactions between the variables are shown in Figures 6 to 10. The response surface curves were plotted to understand the interaction of the variables and to determine the optimum level of each variable for maximum response. The elliptical shape of the curves indicates good interaction of the two variables and circular shape indicates no interaction between the variables. The curves obtained in this study showed that there is relative significant interaction between all the variables. Optimum conditions of Pb(II) removal by activated carbon were also obtained from the response surface plots.

The stationary point or central point is the point at which the slope of the contour is zero in all directions. The coordinates of the central point within the highest contour levels in each of the plots will correspond to the optimum values of the respective variables. The maximum predicted metal ions removal is indicated by the surface confined in the smallest curve of the contour diagram. The optimum values of the variables were: temperature, 50^0C; contact time, 87.83mins; adsorbent dosage, 1.32g/L and pH, 6.04.

Table 4: Analysis of variance (ANOVA) for the fitted quadratic polynomial model

Source of variables	Coefficient estimate	Degree of freedom	Sum of squares	F-value	P-value (Prob >F)
Model	93.500	14	1061.55	48.30	< 0.0001
A-Temperature	3.771	1	341.26	217.37	< 0.0001
B-Contact time	1.622	1	63.12	40.20	< 0.0001
C-Adsorbent dosage	1.733	1	72.11	45.93	< 0.0001
D- Solution pH	-0.379	1	3.45	2.20	0.1589
AB	-0.944	1	14.25	9.08	0.0087
AC	0.544	1	4.73	3.01	0.1031
AD	0.920	1	13.54	8.63	0.0102
BC	1.005	1	16.16	10.29	0.0059
BD	0.281	1	1.27	0.81	0.3834
CD	0.744	1	8.85	5.64	0.0314
A^2	-2.523	1	174.53	111.17	< 0.0001
B^2	-3.735	1	382.63	243.72	< 0.0001
C^2	-1.780	1	86.90	55.35	< 0.0001
D^2	-0.698	1	13.34	8.50	0.0107
Residual		15	23.55		
Lack of fit		10	20.05	2.86	0.1285
Pure Error		5	3.50		
Cor. Total		29	1085.10		

Std. Dev. = 1.253; Mean = 86.512; C.V.% = 1.45; PRESS = 120.53; R^2 = 0.9783;
Adj. R^2 = 0.9580; Pred. R^2 = 0.8889; Adeq. Precision = 21.157

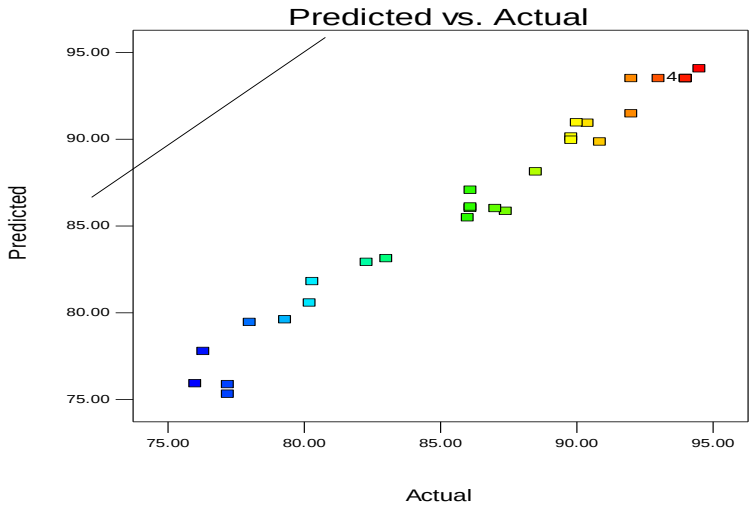

Fig. 4: Plot of the predicted adsorption efficiency versus the actual experimental value

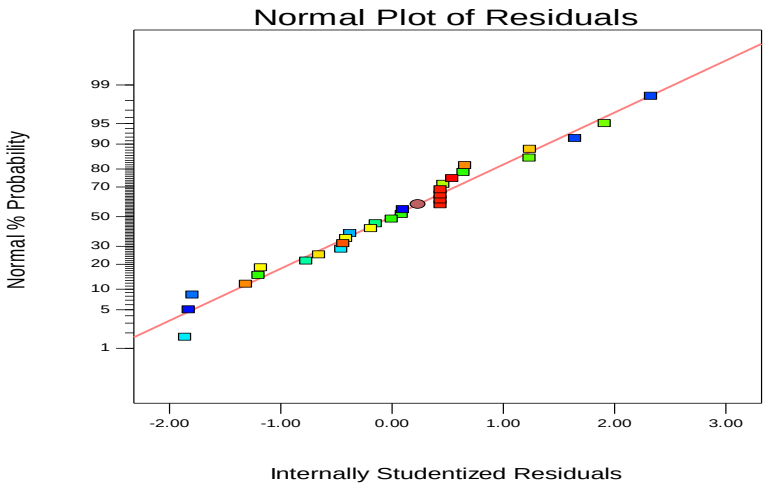

Fig. 5: Normal probability plot of the residual

The predicted response value of Pb(II) removal at these optimum values was 95.58%. To confirm this optimum values, experiments were performed at these values and the experimental response value of Pb(II) removal was 94.83 %. This showed that the model correctly explains the influence of the process variables on the Pb(II) adsorption from aqueous solution by PMAC.

The lack of fit test with p-value of 0.1285, which is not significant (p-value >0.05 is not significant) showed that the model satisfactorily fitted to the experimental data. Insignificant lack of fit is mostly needed because significant lack of fit indicates that there might be contributions in the regression response relationship that is not accounted for by the model. The predicted values versus actual values for the Pb(II) removal with adjusted R^2 value of 0.9580 shows the model with 95.80% of variability (Fig. 4). The predicted value and the experimental values were in reasonable agreement (R^2 close to unity), which means that the data fit well with the model and give a convincingly good estimate of response for the system in the range studied. In addition, investigation on residuals to validate the adequacy of the model was performed. Residual is the difference between the observed response and predicted response. This analysis was examined using the normal probability plot of residuals (Fig. 5) and the plot of the residual versus the normal probability plot of the residuals shows that the errors are distributed normally in a straight line and insignificant.

On the other hand, the plot of residuals versus predicted response showed a structure less plot suggesting that the model is adequate and that the model does not show any violation of the independence or constant variance assumption hence conforming to the literature by [18].

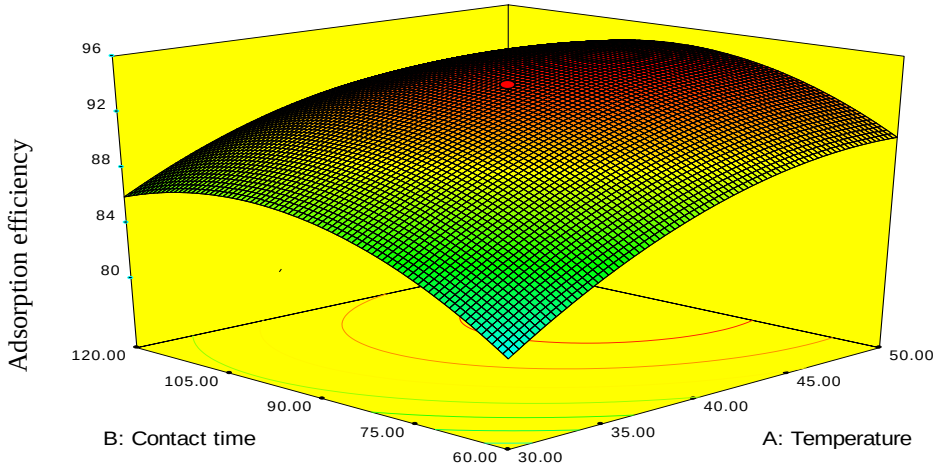

Fig. 6: Surface plot between contact time and temperature against adsorption efficiency of Pb(II)

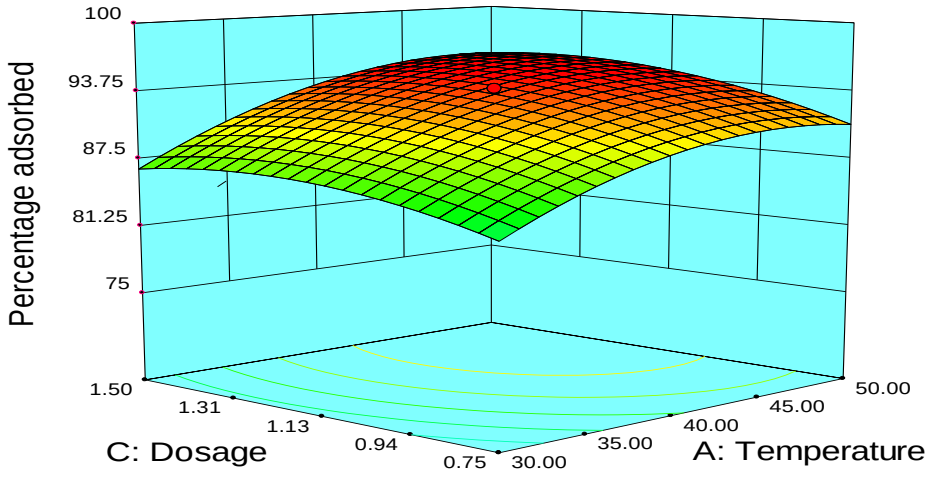

Fig. 7: Surface plot between adsorbent dosage and temperature against adsorption efficiency of Pb(II)

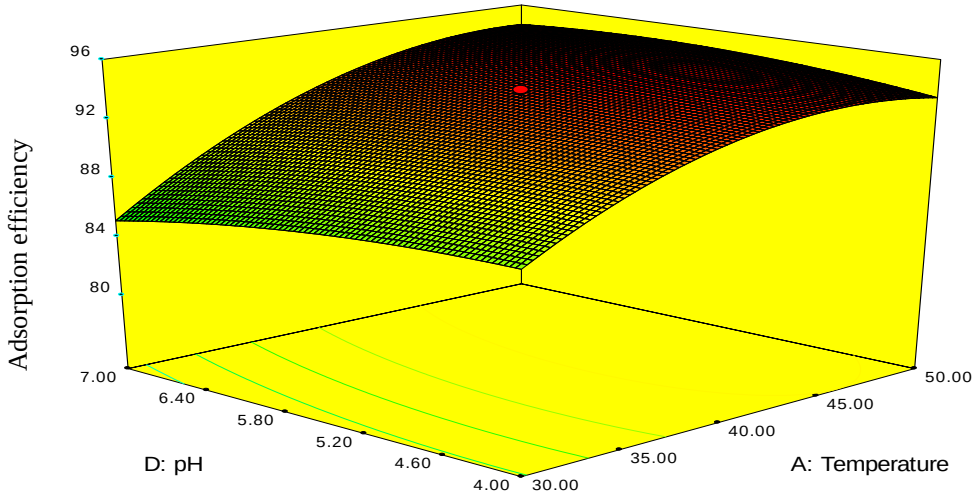

Fig. 8: Surface plot between pH and temperature against adsorption efficiency of Pb(II)

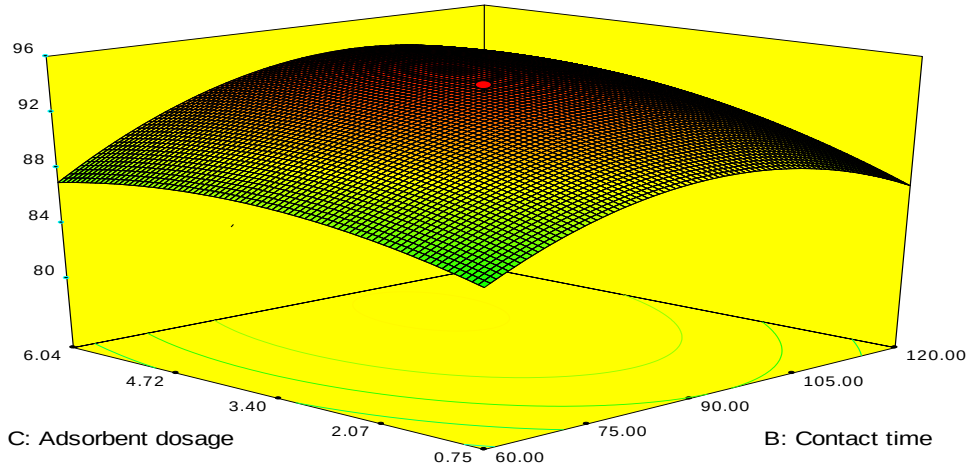

Fig. 9: Surface plot between adsorbent dosage and contact time against adsorption efficiency of Pb(II)

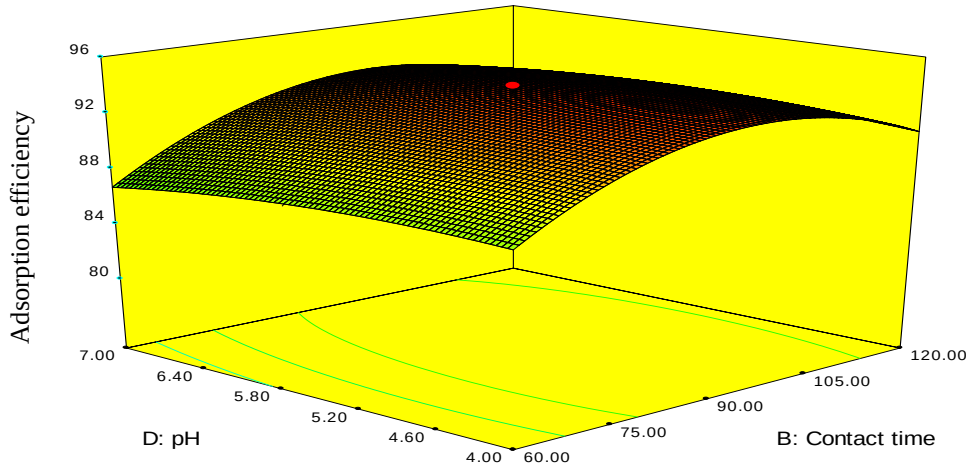

Fig. 10: Surface plot between contact time and pH against adsorption efficiency of Pb(II)

IV. CONCLUSIONS

In this work a study of the optimization of activated carbons from pentaclethra Macrophylla (PMAC) seed shells for the removal of Pb(II) from aqueous solution was carried out by response surface methodology (RSM). The process parameters for adsorption such as: particle size, adsorbent dosage, initial pH of solution, initial Pb(II) concentration, temperature and contact time were investigated. The analysis of variance (ANOVA) showed that a satisfactory result was obtained. Furthermore, increasing both time and adsorbent dosage higher adsorption rate was achieved and solution concentration does not seem to have any significant effect. The statistical models developed for predicting yield showed a good agreement between the experimental and calculated values (≥ 0.96), demonstrating the usefulness of regression analysis as a tool for optimization purposes. The experimental results suggested the optimal condition as follows: solution temperature, 30^0C; contact time, 120minutes; adsorbent dosage, 1.50 g; and pH, 7. This optimized condition was validated with the actual removal efficiency in 96%.

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