

# Modeling and Optimization of Adsorption of Heavy Metal Ions onto Local Activated Carbon

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### **Abstract**

In this study, a mathematical model was constructed according toCentral Composite Design method (CCD), which simulated the experimental work for adsorption of  $(Cu^{2+}, Fe^{3+}, Pb^{2+})$ and  $\text{Zn}^{2+}$ ) in batch adsorption processes, where this model was studied the different effects of operational conditions and their impact on the efficiency of adsorption by using activated carbon produced from rice husk as local raw material which is low cost and available in huge quantities,and find a final form simulates practical experiences. Finally a mathematical model has been used as a software program (minitab16).

**Keyword:** Activated carbon, Adsorption, Modeling, Design of experiments, Heavy metal ions, Rice husk, Central composite design



# **1. Introduction**

Heavy metal ions such as copper, iron, nickel, lead, etc. in the environment are of major concern due to their toxicity to many life forms. Unlike organic pollutants, which are susceptible to biological degradation, metal ions do not degrade into any harmless end products (Mohammadiet al., 2010) and tend to accumulate causing several diseases and health disorders in humans, and other living organisms (Rosa et al., 2008). Several industrial activities are important sources ofenvironmental pollution due to their high content of several heavy metal ions(Dada et al., 2012). Wide range of various treatment techniques available for the removal of heavy metal ions from aqueous solutions such as ion exchange, biodegradation, oxidation, solvent extraction, chemical precipitation, flotation, biosorption, electrolytic recovery, membrane separation and adsorption have been reported to be used for removal of heavy metal ions from industrialeffluents (Al-tameemi et al., 2012; Deosarkar,2012). However, adsorption has been universally accepted as one of the most effective pollutant removal process, with low cost, ease in handling, low consumption of reagents, as well as scope for recovery of value added components through desorption and regeneration of adsorbent(Dada et al., 2012). Adsorption is collection of adsorbate on the surface of adsorbent due to force of attraction(Deosarkar,2012). The practical applications of adsorption can be at separation and purification of liquid and gas mixtures, bulk chemicals, drying gases and liquids before loading them into industrial systems, removal of impurities from liquid and gas media, recovery of chemicals from industrial and vent gases and water purification(Prabakaran&Arivoli,2012). Activated carbon is the most widely used adsorbent due to its excellent adsorption capability for heavy metals. However, the use of these methods is often limited due to the high cost, which makes them unfavorable for the needs of developing countries. Many reports have been investigatedthe low-cost adsorbents for Adsorption of heavy metals from aqueous solutions(Souag et al., 2009)such as date pits(Belhachemi et al., 2009) bamboo(Kannan&Veemaraj, 2009) oil palm fibre(Hameedet al., 2011;Nwabanne&Igbokwe, 2012), coconut shell(Satya et al., 1997), apricot stones (Philip&Girgis, 1996), sugar beet bagasse (Jaguaribe et al., 2000), waste tires(Teng et al., 2000;Juan et al., 2005;Mui et al., 2010), coconut husk, seed shell (Gueu et al.,2006), dates stones (Alhamed&Bamufleh, 2008), sun flower (Surchi, 2011), asphaltic carbon(Ambursa et al., 2011), Henna Leaves (Shanthi&Selvarajan, 2012).The intrinsic properties of activated carbon are dependent on the raw material source. The source of raw material was based on the need for developing low cost absorbent for pollution control as well as reducing the effect of environmental degradation poised by agricultural waste(Itodo H. &Itodo A., 2010).

In this study, a simulation of batch adsorption processes was investigated by mathematical model for adsorption of heavy metal ions such as  $(Fe^{3+}, Zn^{2+}, Cu^{2+}$  and  $Pb^{2+})$  from the (oil-water)polluted which comes out from the oil industry in Basrah cityonto activated carbon produced from rice husk (RHAC) as local raw material which is low cost and available in huge quantities causing a pollutant problem.



# **2.Experimental Section**

# *2.1 Materials*

Zinc chloride with purity (97%) and sodium hydroxide with purity (97.5%) were supplied from THOMAS BAKER (Chemicals) Company. Copper chloride anhydrous with purity (99%) was supplied from BDH(Chemicals) Company. Iron nitrate (ferric nitrate) with purity (99%) was supplied from MERCK Company. Hydrogen chloride with purity (37%) was supplied from Scharlab.S.L Company. Nitrogen gas with purity (90%)and carbon dioxide gases with purity (95 - 99 %)were supplied from Basrah Factory. Rice husks were collected from Almshgab City Al-najafALashraf, Iraq, which had been discarded as waste from rice cultivation.

# *2.2 Adsorbent*

Activated carbon produced from rice husk (RHAC) by physical method was used as an adsorbent material in this study, the preparation method was described following:

Initially, the (RH) were well washed with distilled water and dried in electrical oven for 24 hours. The carbonization step was carried out in electrical furnace for 2hr at 500C and heating rate of 30 °C/min in absence air using nitrogen  $(N_2)$  at flow rate is 200 L/min.

In the activation step, the product from carbonization step was activated by passing carbon dioxide  $(CO_2)$  instead of nitrogen for 2hr at 700C.

# *2.3Preparation of Standard Solutions*

The stock solutions of 1000 mg/L (ppm) of  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  were prepared by dissolving 2.1368 g of CuCl<sub>2</sub>, 7.3073 g ofFe(NO<sub>3</sub>)<sub>3</sub>, 1.3557 g ofPbCl<sub>2</sub>and2.1273g ofZnCl<sub>2</sub> in 1000 ml volumetric flasks and fill up to the mark with distilled water.

The diluted concentrations were prepared from stock solutions for carrying out experiments.

A certain volume (10 ml) of oil has been added to all above solutions with efficient agitation for simulated waste oil water.

# *2.4Analyze a Sample of Heavy Metal Ions by Using Atomic Absorption Spectrophotometer (AAS)*

The concentration of metal ions was measured by using atomic absorption spectrophotometer (BUCK Scientific, Model 210 VGP). In atomic absorption spectroscopy, metal atoms were vaporized into a flame, and the metal vapor absorbed radiation from the specific hollow cathode lamp in proportion to the number of atoms present. Beer's Law was followed in the part-per-million range (remember that ppm means mg of metal/liter of solution).

# *2.5Adsorption Studies*

Batch experiments were carried out by a (125 ml) flask. A certain weight of adsorbent material and (100 ml) of the solution prepared previously were added to the flask, and installed in the water bath (MemmertGmbh Type WMB 22) at different temperature, see



Figure1. The pH values were controlling by adding 0.1 N NaOH or 0.1 N HCl.A mixture with a different speed was mixed for 15 minutes using Variable-Speed Benchtop, model 5850, Eberbach. Finally, the mixtures were filtered through filter paper, and measurement of concentrations by Atomic Absorption.



Figure 1. Schematic diagram of the batch adsorber (Al-Jomaa, 2011)

The removal percentage (R.P.%) which described the efficiency of adsorbent to adsorbed a heavy metal ions is calculated by following equation (BADMUS et al., 2007; Itodo et al., 2010):

$$
R.P. \% = \frac{c_i - c_f}{c_i} * 100
$$
 (1)

Where: $C_i$  and  $C_f$  are the initial and final concentration in (ppm), respectively.

# **3. Results and Discussion**

# *3.1 Modeling of Heavy Metal Ions Adsorption*

Design of experiments (DOE) methods all involve: (1) carefully planning sets of input combinations to test using a random run order; then, (2) tests are performed and output values are recorded; (3) an interpolation method such as "regression" is then used to interpolate the outputs; and (4) the resulting prediction model is then used to predict new outputs for new



possible input combinations, DOE methods can be an important part of systemoptimization.These methods all involve the activities of experimental planning, conducting experiments, and fitting models to the outputs(Allen, 2006).

DOE methods are classified into several types, which included screening using fractional factorials, response surface methods (RSM), and robust design procedures.All of these DOE methods involve changing key input variable settings which are directly controllable (called factors) using carefully planned patterns, and then observing outputs (called responses) (Allen, 2006).

Response surface methodology is a collection of statistical and mathematical methods that are useful for the modeling and analyzing engineering problems. In this technique, the main objective is to optimize the response surface that is influenced by various process parameters. Response surface methodology also quantifies the relationship between the controllable input parameters and the obtained response surfaces (Tanet al., 2007; Aslan & Cebeci, 2007).

The particular value of the variable is called the level of the factor. The combination of factors used in a particular experiment is called a treatment (Al-Badran, 2003; Ghadeer, 2009).

RSM methods are based on three types of design of experiments (DOE) matrices. First, central composite designs (CCD) are matrices corresponding to (at most) five level experimental plans from Box and Wilson (1951). Second, Box Behnken designs (BBD) are matrices corresponding to three level experimental plans from Box, Behnken (1960). Third, Allen et al. (2003) proposed methods based on so-called expected integrated mean squared error optimal (EIMSE-optimal) designs (Allen, 2006).

**In this study,** the central composite design was used to determine a models which described therelationship between the variables and the response.

The response which is the product (Y), is assumed to be a random variable (Lazic, 2004).

$$
Y = f(X_1, X_2, X_3) + Error
$$
 (2)

Asecond degree polynomial equation was used if there is a curvature in the system ,which given by Eq.(3) (Chen et al., 2011; Song et al., 2012; Daffalla et al., 2012):

$$
Y_{b} = \beta_{\circ} + \sum_{i=1}^{k} \beta_{i} X_{i} + \sum_{i=1}^{k} \beta_{ii} X_{i}^{2} + \sum_{i(3)
$$

Where:

 $Y_b$ ,  $X_i$ ,  $\beta$ <sup>o</sup>,  $\beta_i$ ,  $\beta_{ii}$ ,  $\beta_{ij}$  and  $X_i$ , *j* are the predicted response, independent variables, model constant,linear coefficients, the quadratic coefficients and cross product coefficients,the coded values of variables, respectively.

These second –order designs for k factors are composed of three sets of points (John, 1998):

(i)A 2<sup>K</sup> factorial design with $X_i = \pm 1$ , these are called the cube points. There are n<sub>j</sub> of term.



(ii) A set of axial points. There are  $n_{\alpha} = 2k$ . There coordinates are  $(\pm \infty, 0, 0, ...), (\dots, 0, \pm \infty)$  $(0, \ldots)$  and  $(\ldots, 0, 0, \pm \alpha)$ , where  $\alpha$  is the distance of the axial point from center and makes the design rotatable(Tanet al., 2007).

(iii)  $n_0$  center points, which used to determine the experimental error and the reproducibility of the data.

The number of experiments (N) needed was calculated by thefollowing equation (Lazic, 2004; John, 1998):

$$
N = n_j + n_\alpha + n_0 = 2^k + 2^k k + n_0 \tag{4}
$$

For five factors a second order polynomial mathematical model is describe by the following equation:

$$
Y_b = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{55} X_5^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{15} X_1 X_5 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{25} X_2 X_5 + \beta_{23} X_3 X_4 + \beta_{35} X_3 X_5 + \beta_{45} X_4 X_5
$$
\n(5)

The relationship between the coded levels and the corresponding actual variables is represented by the equation:

$$
X_{coded} = \frac{(x_{actual} - x_{center})}{(x_{center} - x_{minimum})}
$$
(6)

The low and height values of each variable in batch systemwere listed in Table 1:

Variable	Simple	Low	Height	
PH	$X_1$			
TemperatureC	$\Lambda_2$		50	
Doseg	$X_3$			
Concentration ppm	$X_4$		50	
rpm	Λς	350	750	

Table 1. The low and height values of variables in batch system

The relationship between the coded variable  $(X)$  and the corresponding real variable $(x)$  as following :

$$
X_1 = \frac{(x_1 - 7)}{2}, X_2 = \frac{(x_2 - 36)}{14}, X_3 = \frac{(x_3 - 3)}{1}
$$

$$
X_4 = \frac{(x_4 - 35.5)}{14.5}, X_5 = \frac{(x_5 - 550)}{200}
$$
(7)

The central composite design can be made to be rotatable by choosing  $\alpha = 2^{K/4}$  when a complete factorial is used.For five factors:

$$
\alpha = 2^{5/4} = 2.378\tag{8}
$$



l, 



Table 2. The coded  $&$  uncoded (actual)values of variables in batch system



The regression coefficients are determined by equations (Lazic, 2004):

$$
\beta_{0=a_1} \sum_{1}^{N} Y_b - a_2 \sum_{1}^{K} \sum_{1}^{N} X_i^2 Y_b
$$

$$
\beta_{i=a_3} \sum_{1}^{N} X_i Y_b
$$

$$
\beta_{ij=a_4} \sum_{1}^{N} X_i X_j Y_b
$$

$$
\beta_{ii=a_5} \sum_{1}^{N} X_i^2 Y_b + a_6 \sum_{1}^{K} \sum_{1}^{N} X_i^2 Y_b - a_7 \sum_{1}^{N} Y_b \tag{9}
$$

Where:  $a_1$  ... ... .  $a_7$  are coefficients as determined from Table 3.

Table 3. Coefficients values  $a_1$  ...  $a_7$ 



The results of experimental work of adsorption  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  ions onto RHACin batch processes are listed in Table A.1 Appendix A.

For  $Cu^{2+}$  ions were adsorbed on the RHAC in batch process:

Table 4. The calculated regression coefficients for  $Cu^{2+}$  ions

No.	$Y_b$	$X_1Y_b$	$X_2Y_b$	$X_3Y_b$	$X_4Y_b$	$X_5Y_b$	$X_1X_2Y_b$	$X_1X_3Y_b$
1	81.23938	81.23938	81.23938	81.23938	81.23938	81.23938	81.23938	81.23938
2	84.54624	$-84.5462$	84.54624	84.54624	84.54624	84.54624	$-84.5462$	$-84.5462$
3	74.00122	74.00122	$-74.0012$	74.00122	74.00122	74.00122	$-74.0012$	74.00122
4	76.60166	$-76.6017$	$-76.6017$	76.60166	76.60166	76.60166	76.60166	$-76.6017$
5	69.63233	69.63233	69.63233	$-69.6323$	69.63233	69.63233	69.63233	$-69.6323$
6	73.71796	$-73.718$	73.71796	$-73.718$	73.71796	73.71796	$-73.718$	73.71796
7	64.84563	64.84563	$-64.8456$	$-64.8456$	64.84563	64.84563	$-64.8456$	$-64.8456$
8	67.21829	$-67.2183$	$-67.2183$	$-67.2183$	67.21829	67.21829	67.21829	67.21829
9	90.37154	90.37154	90.37154	90.37154	$-90.3715$	90.37154	90.37154	90.37154
10	92.9487	-92.9487	92.9487	92.9487	-92.9487	92.9487	-92.9487	-92.9487
11	85.91279	85.91279	$-85.9128$	85.91279	$-85.9128$	85.91279	-85.9128	85.91279
12	87.62928	$-87.6293$	$-87.6293$	87.62928	$-87.6293$	87.62928	87.62928	$-87.6293$
13	80.79923	80.79923	80.79923	$-80.7992$	$-80.7992$	80.79923	80.79923	$-80.7992$
14	82.03279	$-82.0328$	82.03279	-82.0328	$-82.0328$	82.03279	$-82.0328$	82.03279





Table 4.Continued





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Table 4.Continued







Table 4.Continued



The adequately of regression model have been checked with Fisher's  $(F_R)$ value and tabular value  $(F_T)$  by following equations:

$$
F_R = \frac{S_{AD}^2}{S_Y^2} \tag{10}
$$

For calculation of  $S_{AD}^2$ , the expression:

$$
S_{AD}^{2} = \frac{SS_{R} - SS_{E}}{f_{AD}} = \frac{\sum_{1}^{N} (Yb - \hat{Y}m)^{2} - (Y\circ j - \overline{Y}\circ)^{2}}{N - (n \circ -1) - \lambda}
$$
(11)

$$
S_{\overline{Y}}^2 = \frac{S_Y^2}{N} \tag{12}
$$

$$
S_{\overline{Y}}^2 = \frac{\sum_{1}^{n\circ} (Y_{\circ j} - \overline{Y}_{\circ})^2}{n\circ - 1}
$$
 (13)

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Knowledge of  $S_{AD}^2$  and  $S_{\overline{Y}}^2$  facilitates determination of both calculating the value of Fisher's

criterion and simultaneously of the tabular value by which we may compare and accept or reject the hypothesis of lack of fit of the regression model.

Where:

 $SS_E$  is sum of squares of reproducibility variance.

 $SS_R$  is residual sum of squares.

 $Y_h$  is outcome of each trial.

Ym is calculated response value from regression equation.

 $Y_{\sigma i}$  is the outcome of one trial in null point.

 $\overline{Y}_o$  is average of replications in null point.

The rotatability conditions is defined by following relations:

$$
f_{AD} = N - \lambda - (n_0 - 1) \tag{14}
$$

For second order regression models:

$$
\lambda = \frac{(K+2)(k+1)}{2} \tag{15}
$$

The value degree of freedom  $(f_E)$  is calculated by following equation:

$$
f_E = N(n-1) \tag{16}
$$









A tabular value  $F_T$  is obtained for  $f_{AD} = 22$  and  $f_E = 52(10-1) = 468$  and  $1-\alpha = 99\%$ , from Table A.2 in Appendix A (Lazic, 2004).

The regression model is adequate with 99% confidence because  $F_R \le F_T$  (Fisher's value  $\le$ tabular value).

A check of significance of regression coefficients is brought down to determining their confidence intervals and their comparison to absolute values of regression coefficients. The rule is (Lazic, 2004):

A regression coefficient is statistically significant if its absolute value is higher than the confidence interval.

When estimating the significance of regression coefficients, these equations are used:

$$
S_{\beta^{\circ}}^2 = \frac{2A\lambda(K+2)}{N} S_{\overline{Y}}^2
$$
 (17)

$$
S_{\beta i}^2 = \frac{S_Y^2}{N - n_0} \tag{18}
$$

$$
S_{\beta ij}^2 = \frac{C^2}{N} S_{\overline{Y}}^2
$$
 (19)

$$
S_{\beta ii}^{2} = \frac{AC^{2}[(K+2)\lambda - (K-2)]}{N} S_{\overline{Y}}^{2}
$$
 (20)

$$
A = \frac{1}{2\lambda[(K+2)\lambda - K]}
$$
 (21)

$$
C = \frac{N}{N - n^{\circ}}\tag{22}
$$

Where:

 $S_{\beta^{\circ}}$ ,  $S_{\beta_1}$ ,  $S_{\beta_{ij}}$  and  $S_{\beta_{ii}}$  are variance of regression coefficients which associated error mean squares in determining regression coefficients  $\beta$ <sup>o</sup>,  $\beta$ <sub>i</sub>,  $\beta$ <sub>ii</sub> and S<sub> $\beta$ <sub>ii</sub>.</sub>

In the case of second-order designs of regression coefficient significances, they are checked by using:





Table 6.  $\Delta \beta_{\circ}$ ,  $\Delta \beta_i$ ,  $\Delta \beta_{ij}$  and  $\Delta \beta_{ii}$  values

A check of statistical significance of regression coefficients indicates that regression coefficients  $\beta$ ,  $\beta_1$ ,  $\beta_{23}$ ,  $\beta_{24}$ ,  $\beta_{11}$ ,  $\beta_{22}$ ,  $\beta_{33}$  and  $\beta_{55}$  are statistically significant, while the other coefficients are insignificant.The final form of the second order regression model with 99% confidence may be given in the form:

$$
Y_b = 96.433 - 1.828X_1 + 2.494X_2 + 6.003X_3 - 4.491X_4 + 0.691X_5 - 6.818X_1^2 - 1.051X_2^2 - 3.602X_3^2 - 1.5311X_5^2 + 0.752X_2X_3 + 0.781X_2X_4 \tag{23}
$$

The same above calculations method are used to determine the models of  $Fe^{3+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  in batch process. The regression coefficients and final model equations are show below.

For  $Fe^{3+}$  ions were adsorbed on the RHAC in batch process:

$\beta_1$ 1.544	3.275	6.2902	$-4.071$	0.458	-5.782	$-0.689$	$-2.315$	0.1423	-1.383 $\beta_{45}$	β
0.252	$-0.50$	0.021	0.175	$-0.071$	0.348	$-0.155$	2.007	0.073	0.064	93.962
$\overline{\mathbf{Y}}_0$		$S_{\overline{v}}^2$		$S_{AD}^2$	$S_{\rm Y}^2$		$F_R$	$f_{AD}$	$f_E$	$F_T$
94.06706		1.9549847		31.14317	101.6592		0.306349	22	468	2.31

Table 7. The calculated regression coefficients for  $Fe<sup>3+</sup>$  ions

A check of statistical significance of regression coefficients indicates that regression coefficients  $\beta$ ,  $\beta_1$ ,  $\beta_{13}$ ,  $\beta_{34}$ ,  $\beta_{11}$ ,  $\beta_{33}$  and  $\beta_{55}$  are statistically significant, while the other coefficients are insignificant. The final form of the second order regression model with 99% confidence may be given in the form:

$$
Y_b = 93.962 + 1.544X_1 + 3.275X_2 + 6.2902X_3 - 4.071X_4 + 0.458X_5 - 5.782X_1^2 - 2.315X_3^2 - 1.383X_5^2 + 0.752X_1X_3 + 0.781X_3X_4
$$
 (24)



For  $Pb^{2+}$  ions were adsorbed on the RHAC in batch process:

$\beta_1$ $-1.564$	1.609	5.722	$-4.82$	0.827	$-1.175$		0.361	$-3.078$	0.9606		$-0.6859$
									$\beta_{45}$		β
0.1344	$-0.26$	0.454	$-0.074$	0.187	0.148	0.05385	1.579	0.115	0.021		88.92243
$\overline{\mathbf{Y}}_0$		$S_{\overline{v}}^2$		$S_{AD}^2$		$S_Y^2$	$F_R$		$f_{AD}$	$f_E$	$F_T$
88.79165		4.0477878		44.59781	210.485		0.211881		22	468	2.31

Table 8. The calculated regression coefficients for  $Pb^{2+}$  ions

A check of statistical significance of regression coefficients indicates that regression coefficients  $\beta$ ,  $\beta_1$ ,  $\beta_2$ ,  $\beta_{33}$  and  $\beta_{34}$  are statistically significant, while the other coefficients are insignificant. The final form of the second order regression model with 99% confidence may be given in the form:

$$
Y_b = 88.922 - 1.564X_1 + 1.609X_2 + 5.722X_3 - 4.82X_4 + 0.827X_5 - 1.175X_1^2 - 3.078X_3^2 + 1.579X_3X_4
$$
\n(25)

For  $\text{Zn}^2$ <sup>+</sup>ions were adsorbed on the RHAC in batch process:

$\beta_1$ 5.467	2.961	7.053	$-8.78$	0.424	$-5.396$	$-0.35678$		$-2.539$	1.1253	$-1.882$
									$\beta_{45}$	β
0.3605	$-0.28$	1.583	$-0.336$	0.166	0.817	0.0218	$-1.14$	0.194	0.277	73.368
$\overline{\mathbf{Y}}\text{.}$		$S_{\overline{v}}^2$		$S_{AD}^2$	$S_Y^2$		$F_R$		$f_E$ $f_{AD}$	$F_T$
73.89135		2.9076597		57.52014	151.1983		0.380428	22	468	2.31

Table 9. The calculated regression coefficients for  $Zn^{2+}$  ions

A check of statistical significance of regression coefficients indicates that regression coefficients  $\beta$ ,  $\beta_1$ ,  $\beta_{14}$ ,  $\beta_{24}$ ,  $\beta_{34}$ ,  $\beta_{11}$ ,  $\beta_{33}$ ,  $\beta_{44}$  and  $\beta_{55}$  are statistically significant, while the other coefficients are insignificant. The final form of the second order regression model with 99% confidence may be given in the form:



 $Y_b = 73.368 + 5.467X_1 + 2.961X_2 + 7.053X_3 - 8.78X_4 + 0.424X_5 - 5.396X_1^2$  $2.539X_3^2 + 1.1253X_4^2 - 1.882X_5^2 + 1.583X_1X_4 + 0.817X_2X_4 - 1.14X_3X_5$  (26)

# *3.2Modeling Using Minitab Software*

Minitab is a statistical software, it was developed by Minitab Inc. (USA).Minitab16.1.0, was used in this study to determine the models of adsorption of heavy metal ions on RHAC.

The calculations and results of models which were determined by this program are listed in Appendix (B), clarification and explanation of the tables and calculations are shown below.

The coefficients table is listed the estimated coefficients for the variables.

Regression examines the relationship between a response and variables. In order to determine whether or not the observed relationship between the response and variables is statistically significant, need to:

Identify the coefficient p-values: the coefficient value for P (p-value) tells whether or not the association between the response and variables is statistically significant. Compare the coefficient p-values to  $\alpha$ -level: if the p-value is smaller than the  $\alpha$ -level, the association is statistically significantly.

P regression was used to test the hypothesis that all the coefficients in the model are zero. A smaller p-value than a pre-selected selected  $\alpha$ -level implies that at least one coefficient in the model is not zero.

P lack of fit was used to test whether the model fits the data well. A smaller p-value than α-level indicates that might need to consider higher order terms of existing predictors, or additional predictors, to get a better fit of the data.

A list of the standard errors for the estimated constant and the estimated coefficient. A standard error for an estimated coefficient measures the precision of the estimate. The smaller the standard error, the more precise the estimate.

S is measured in the units of the response variable and represents the standard distance data values fall from the regression line. For a given study, the betterequation that predicts the response, the lower S is.

Minitab displays the coefficients in uncoded units in addition to coded units. For each term in the model, there is a coefficient. Use these coefficients to construct an equation representing the relationship between the response and the factors.

To use this equation, put in the uncoded (actual) factor values and calculate the variables response. Because these coefficients are estimated using uncoded units, putting coded factor values into this equation would produce incorrect predictions about yield.

Note: the above clarification and explanationwere quoted from the help of program.

The final model equations were calculated by this program are shown below:



For  $Cu^{2+}$  ions were adsorbed on the RHAC in batch process:

$$
Y_b = 96.3394 - 1.8273X_1 + 2.4932X_2 + 6.0X_3 - 4.489X_4 - 7.41X_1^2 - 1.6345X_2^2 - 4.189X_3^2 - 2.1146X_5^2
$$
\n(27)

For  $Fe^{3+}$  ions were adsorbed on the RHAC in batch process:

$$
Y_b = 93.868 + 1.543X_1 + 3.27X_2 + 6.28X_3 - 4.069X_4 - 6.38X_1^2 - 1.278X_2^2 - 2.906X_3^2 - 1.973X_5^2 + 2.01X_3X_4
$$
\n(28)

For  $Pb^{2+}$  ions were adsorbed on the RHAC in batch process :

$$
Y_b = 88.827 - 1.56X_1 + 1.608X_2 + 5.7198X_3 - 4.82X_4 - 1.778X_1^2 - 3.684X_2^2 - 1.288X_5^2
$$
\n(29)

For  $\text{Zn}^2$  ions were adsorbed on the RHAC in batch process:

$$
Y_b = 73.295 + 5.464X_1 + 2.96X_2 + 7.049X_3 - 8.781X_4 - 5.855X_1^2 - 2.993X_3^2 - 2.3357X_5^2
$$
\n(30)

### *3.3Validity of Models*

Thevalidity of each equations of model can be tested by the Sum of Squared Errors (SSE %), the sum of squared errors was determined by following (Tanet al., 2007):

$$
SSE\% = \sqrt{\frac{\Sigma (RP_{exp} - RP_{cal})^2}{N}}
$$
(31)

The lower value of SSE is indicate the better, which indicates that the best model can be chosen.

Table 10. The values of sum of squared errors

H.M.I.	$Cu^{2+}$		$Fe^{3+}$		$Ph^{2+}$		$\mathbf{Zn}^{2+}$	
		Models CCD Minitab CCD Minitab CCD Minitab CCD Minitab						
		<b>SSE</b> % 4.252 3.370 3.676 2.523 4.304 6.715					4.983 4.973	

Where:

N is the number of data points.  $RP_{\text{exp}}$  is the values of removal percentage from experimental work.  $RP_{cal}$  is the values of removal percentage which calculated from models.H.M.I. is heavy metal ions.



# **4. Conclusion**

A mathematical model wasconstructedaccording to Central Composite Design method (CCD) and a software program (minitab16). These models were simulated experimental work for adsorption of  $(Cu^{2+}, Fe^{3+}, Pb^{2+}$  and  $Zn^{2+})$  in batch adsorption processes using activated carbon produced from rice husk as local raw material which is low cost and available in huge quantities causing a pollutant problem. Final modeling equations were well simulated experimental work with very little deviation by Fisher's testing (1%), as well as the results of equations derived using (minitab16).

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# **Appendix**

Appendix A.1. The experimentalresult of adsorption of heavy metalions on the RHAC





31	9	22	2	21	350	77.64412	81.06704	82.68977	66.5229
32	5	22	$\overline{2}$	21	350	79.86298	76.30535	84.87837	55.21746
33	2.243	36	3	35.5	550	65.16427	53.23355	82.7634	33.13241
34	11.76	36	3	35.5	550	47.34202	65.34776	74.23148	56.28086
35	7	2.702	3	35.5	550	84.75804	84.42365	83.76516	67.8024
36	7	69.3	3	35.5	550	93.10076	91.87511	90.64515	78.72574
37	7	36	0.6216	35.5	550	51.82756	58.27698	41.58728	30.38296
38	7	36	5.3784	35.5	550	97.12532	99.60192	93.83991	91.40932
39	7	36	3	1.013	550	100	100	100	98.8141
40	7	36	3	69.99	550	87.49923	85.7259	81.19688	64.50927
41	7	36	3	35.5	74.32	78.67269	79.63733	73.18559	57.88295
42		36	3	35.5	1026	93.75402	88.79539	89.35254	71.35046
43	7	36	3	35.5	550	96.60561	95.66103	89.35254	73.14867
44	7	36	3	35.5	550	96.06727	95.66103	90.96699	74.06098
45	7	36	3	35.5	550	97.94627	93.81068	89.9999	70.46211
46	7	36	3	35.5	550	96.95424	95.98851	88.05152	73.14867
47	7	36	3	35.5	550	97.46075	91.87511	91.28831	75.91122
48	7	36	3	35.5	550	96.2487	92.67749	88.05152	75.91122
49	7	36	3	35.5	550	97.21003	93.52026	84.43038	74.98215
50	7	36	3	35.5	550	96.95424	94.71204	89.9999	72.24541
51	7	36	$\overline{3}$	35.5	550	95.32283	92.95377	87.39786	74.98215
52	7	36	3	35.5	550	95.03638	93.81068	88.37756	74.06098

AppendixA.2.  $F_T$  Values





AppendixB. The calculation and results of models were determined by Minitab program

#### **Central Composite Design**

Replicates:<br>Total runs:<br>Total blocks: 5  $\mathbf 1$ Factors: 52 52 Base runs:  $\mathbf{1}$ Base blocks:  $\mathbf{1}$ Two-level factorial: Full factorial 32 Cube points:  $\overline{10}$ Center points in cube: Axial points:<br>Center points in axial:  $10$  $\mathbf{o}$ 

Alpha: 2.37841

Design Table





# Adsorption of  $Cu^{2+}$  in batch presses

#### Response Surface Regression: response versus X1, X2, X3, X4, X5

The analysis was done using coded units.

Estimated Regression Coefficients for response





Analysis of Variance for response



Unusual Observations for response



R denotes an observation with a large standardized residual.

# *Adsorption of*  $Fe^{3+}$  *in batch presses*

#### Response Surface Regression: Response versus X1, X2, X3, X4, X5

The analysis was done using coded units.

Estimated Regression Coefficients for Response

Term	Coef	SE Coef	т	P
Constant	93.8683	0.9561	98,180	0.000
X1	1.5434	0.4622	3,339	0.002
X2	3.2736	0.4622	7.083	0.000
X3	6.2868	0.4622	13.601	0.000
<b>X4</b>	$-4.0695$	0.4622	$-8.804$	0.000
X5	0.4583	0.4622	0.992	0.329
$X1*X1$	$-6.3800$	0.3976	$-16.045$	0.000
$X2*X2$	$-1.2784$	0.3976	$-3.215$	0.003
$X3*X3$	$-2.9065$	0.3976	$-7.310$	0.000
$X4*X4$	$-0.4452$	0.3976	$-1.120$	0.271
X5*X5	$-1.9737$	0.3976	$-4.964$	0.000
$X1*X2$	0.2524	0.5378	0.469	0.642
$X1*X3$	$-0.5012$	0.5378	$-0.932$	0.359
$X1*X4$	0.0217	0.5378	0.040	0.968
$X1*X5$	0.1760	0.5378	0.327	0.746
$X2*X3$	$-0.0712$	0.5378	$-0.132$	0.896
$X2*X4$	0.3489	0.5378	0.649	0.521
$X2*X5$	$-0.1558$	0.5378	$-0.290$	0.774
$X3*X4$	2.0105	0.5378	3,739	0.001
X3*X5	0.0739	0.5378	0.137	0.892
X4*X5	0.0644	0.5378	0.120	0.905

# $S = 3.04198$  PRESS = 1227.20<br>R-Sq = 95.42% R-Sq(pred) = 80.41% R-Sq(adj) = 92.46%

#### Analysis of Variance for Response



#### Analysis of Variance for Response



#### Unusual Observations for Response



R denotes an observation with a large standardized residual.







# $Adsorption of Pb<sup>+2</sup> in batch presses$

#### Response Surface Regression: Response versus X1, X2, X3,

The analysis was done using coded units.

Estimated Regression Coefficients for Response



Estimated Regression Coefficients for Response using data in uncoded un



# $Adsorption of Zn<sup>+2</sup> in batch presses$

### Response Surface Regression: Response versus X1, X2, X3, X4, X

The analysis was done using coded units.

Estimated Regression Coefficients for Response



 $S = 5.81350$  PRESS = 4679.38<br>R-Sq = 90.52% R-Sq(pred) = 57.64% R-Sq(adj) = 84.40%



 $\overline{\mathbf{P}}$  $0.000$ <br> $0.000$  $0.000$  $0.000$ <br>0.002<br>0.000  $0.000$  $0.634$ <br> $0.000$  $0.000$  $0.296$ <br> $0.000$  $0.380$  $0.004$ <br>0.896<br>0.728  $0.785$ <br> $0.785$ <br> $0.133$  $0.745$  $0.872$  $0.432$  $0.983$  $0.272$  $0.851$  $0.789$  $0.000$ 

 $-2.39 R$  $4.74$  R<br>2.14 R  $2.66 R$ 

uncoded unit



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 $X3*X5$ 

 $X4*X5$ 

0.000974679

9.58348E-05