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Optimizing the Sorption of Mn^{2+} ion from Aqueous Solution onto Zinc Chloride Activated Sawdust Using Response Surface Methodology (RSM)

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Abstract
Activated carbon from sawdust was prepared and characterized using Fourier transform infra-red (FTIR) and scanning electron microscope (SEM) to determine the presence of functional groups and visualize its microstructural arrangement in other to ascertain its potential for the removal of Mn^{2+} ion from aqueous solution. Statistical design of experiment (DOE) using central composite design was then employed to randomized the levels of selected input parameters in order to determine their optimum values that will guarantee maximum adsorption. To optimize the process, response surface methodology based on numerical optimization was employed. The behaviour of the system which was used to evaluate the relationship between the input and the response variables was explained using the empirical second-order polynomial equation. To validate the optimization results, selected goodness of fit statistics, namely; coefficient of determination, adjusted coefficient of determination and predicted coefficient of determination were employed. Results obtained revealed the adequacy of response surface methodology in optimizing adsorption systems. Analysis of variance test revealed that the model developed is significant at 0.05df with computed p-value < 0.0001. Computed goodness of fit statistics revealed that the predicted R^2 value of 0.7998 is in reasonable agreement with the adjusted R^2 value of 0.9062. In addition, numerical optimization results indicate that for 50 mL aqueous solution containing 11.39 mg/L of manganese, 1.0 g zinc chloride activated sawdust, pH of 5.0 and a contact time of 120 minutes will be required to obtain a sorption efficiency of 84.04% with amount removed (qe) of 714mg/g. The outcome of this study justifies the use of sawdust as adsorbent for the treatment of water and wastewater containing divalent metal ions.
Keywords: Response surface methodology, central composite design, ANOVA, numerical optimization.
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1. Introduction

Environmental pollution caused by the discharge of untreated effluents containing toxic metals such as lead, chromium, and manganese has become an issue of concerned and have developed into a widely studied area (Ziemacki et al., 1989). Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products, and their presence in streams and lakes leads to bioaccumulation in living organism, causing health problems in animals, plants and human beings (Weng et al., 2007, Demirbas et al., 2004). The assimilation of relatively small amounts of these heavy metals over a long period of time in the human body can lead to chronic toxicity coupled with numerous health challenges such as skin irritation, lung tumor including severe damage to the nervous systems and circulatory system (DWI, 2014). The toxic effects of lead, chromium and manganese ions in human, especially when present above the threshold limit in the hydrosphere are well documented (Khurshid & Qureshi, 1984). The presence of these heavy metals in the environment is of great concern to scientists and engineers because of their toxic nature (Sekar et al., 2004).

Numerous conventional processes have been developed over the years to remove these heavy metals from water and wastewater they include; solvent extraction, chemical precipitation, ion exchange process, electrolytic precipitation, and reverse osmosis (Izinyon et al., 2016). Except for a few studies in the literature of heavy metal adsorption, only traditional method of experimentation (varying one variable and fixing the others) have been adopted in studying the interacting effect of selected input variables on adsorption process (Jaikumar & Ramamurthi, 2009). This method of experimentation usually give rise to large experimental runs and do not allow for the establishment of the multiple interacting effect of the selected variables. In addition, determining the optimum value of the selected input variables that will guarantee maximum adsorption is almost beyond the scope of traditional method of experimentation. This limitation of traditional method of experimentation can be eliminated by randomizing all the controlling variables using statistical design of experiment (DOE) which allows a large number of factors to be screened simultaneously (Montgomery, 1996). Since adsorption is a complex process that is influenced by numerous independent variables, determining the optimal working condition requires the use of classical methods of optimization which are useful for developing and analyzing processes in which the response of interest is influenced by several independent variables and the main objective is to optimize the

response (Kumar et al., 2010, Cerino-Cordova et al., 2011, Ilaboya & Izinyon, 2019).

In recent years, statistical design of experiment (DOE) and artificial neural network (ANN) has been successfully employed to optimize and predict the sorption efficiency of divalent metals on different adsorbents such as zeolite, electric arc furnace slag, sunflower powder and Zea Mays. Although, artificial neural network (ANN) are one of the many machine learning tools that are capable of performing the task of modelling and prediction of experimental data, determining the optimum values of the input variables required to maximize the efficiency of metal ion removal has continue to pose a challenge to the use of neural network. Following this, response surface methodology (RSM) was employed since they represent a special class of statistical technique which are capable of optimizing a system in which the response of interest is influenced by several input variables. In this study, statistical design of experiment using central composite design method and response surface methodology were used to optimize the sorption of Mn^{2+} from aqueous solution onto zinc chloride activated sawdust with a view to determine the optimum value of selected adsorption variables, namely; initial metal ion concentration, adsorbent dose, contact time and pH that will guarantee maximum adsorption. Sawdust was selected for this study because it is cheap and readily available. It is easy to prepare, highly effective and also non-toxic (Ikenyiri, et al., 2019).

2. Experimental

2.1 Material collection and preparation

Locally available sawdust was collected from sawmill located in Egor Local Govt. Area in Edo State of Nigeria using a washed, clean dried shovel. 2 kg of the sawdust was placed in a fresh black polythene bag and taken to Water Resources and Environmental Engineering Laboratory in the Department of Civil Engineering, University of Benin where the experiment was conducted. First, the sawdust was soaked in a plastic bowl containing 5% hydrogen peroxide and washed with distilled water to remove any carbonaceous and water-soluble impurities. It was dried in hot air oven at 50-70°C for 8 hours, pulverized and screened sieved to obtain geometric sizes of 212 µm before analysis (Mariadas et al., 2012). Carbonization was done using the method recommended by (Ekpete & Horsfall, 2011) with slight modification as follows. 500 g of the pulverized sawdust was placed in a muffle furnace which allows limited supply of air at a temperature of 250^{0C} for 60 minutes. The sample was then placed in a desiccator to cool before it was activated using the method recommended by (Mansfield, 1996) with slight modification as follows: 125 g of the carbonized sawdust was soaked in 250 mL of 5.5M $ZnCl_2$ solution. The mixture was thoroughly mixed until it formed a paste. The paste was then transferred to an evaporating dish which was placed in an oven and heated at 200°C for thirty minutes. It was then allowed to cool and washed with distilled water to remove the residual salt. Thereafter, it was oven dried at 105^0C for thirty minutes, grind using mortar and pestle and sifted with 106µm Standard Tyler Sieve. The activated sawdust was then characterized before using.

2.2 Equipment used for the experiment

Major equipment's used in this study are presented in Table 1. Minor equipment's include: pH meter, digital weighing balance and hand held conductivity meter. Glass wares include: reagent bottles, conical flask, measuring cylinder, glass funnels and beakers.

Table 1: Equipment Details

S/No	Equipment Name	Model
1	Laboratory Oven	DHG 9101-2A
2	Industrial Furnace	DHG 9101-5A
3	Constant Temperature Water Bath	DHG 3101-6A
4	Hot Plate with Magnetic Stirrer	HJ-3D
5	Scanning Electron Microscope (SEM)	APEX 3020 PSEM 2
6	Fourier Transform Infra-red (FTIR)	FTIR 2000, Shimadzu Kyoto, Japan
7	X-Ray Fluorescence (XRF)	APEX 3022
8	Atomic Absorption Spectrophotometer (AAS)	UNICAM SOLAR 969

2.3: Performance of activated sawdust

2.3.1: Analysis of Microstructures

Scanning electron microscope (SEM) was employed to study the surface characteristics in order to assess the presence of microporous structures on the surface of activated sawdust. Such presentations can provide possible explanations on the adsorbent behaviour and its adsorption potentials (Omisanya et al., 2012).

2.3.2 Functional group analysis

Fourier Transform Infra-Red (FT-IR) spectra of activated sawdust was obtained by using FTIR spectrophotometer (Model: FTIR 2000, Shimadzu Kyoto, Japan). The spectra were employed to determine the presence of functional groups that can influence the adsorption capacity of the sawdust. 150 mg potassium bromide (KBr) disks containing approximately 2 % sawdust was prepared prior to recording the FTIR spectra in the range of 400-4000

cm^{-1} with a resolution of 4.0 cm^{-1} (Dawodu et al., 2012).

2.4 Preparation of aqueous solution

Stock solution of manganese was prepared by dissolving accurate quantity of manganese (II) chloride tetrahydrate ($MnCl_2.4H_2O$) in one liter of distilled water. All working solutions were made by diluting the stock solution with distilled water and the concentration of Mn^{2+} ion present in solution was determined with the aid of Atomic Absorption Spectrophotometer (AAS). A duplicate was analyzed for each sample to track experimental error and show capability of reproducing results. The pH of the working solution was adjusted to the desired value for each experiment with drop wise addition of 1 M nitric acid (HNO_3) or 1 M sodium hydroxide (NaOH). A comprehensive list of all the chemicals and reagents with the respective minimum assay is presented in Table 2.

Table 2: List of chemicals and reagents

S/No	Chemicals/Reagents	Type	Minimum Assay
1.	Nitric Acid	Analytical	96 %
2.	Sodium Hydroxide	Analytical	96 %
3.	Manganese (II) chloride tetrahydrate	Analytical	96 %
4.	Hydrogen Peroxide	Analytical	96 %
5.	Zinc chloride	Analytical	96 %

2.5 Adsorption studies

250 mL conical flask containing varying dose of adsorbent and 50 mL aqueous solution of the metal was agitated at 150 rpm using mantle fitted with magnetic stirrer for maximum contact time of 120 minutes. The pH value of aqueous solution was kept at the optimum and separation of adsorbent from aqueous solution was done by filtration using 150 mm whatman filter paper. The filtrate was stored in sample cans and placed in refrigerator prior to analysis. The residual metal ion concentration was determined using Atomic Absorption Spectrophotometer (AAS). Amount of Mn^{2+} ion removed during the series of batch investigation was determined using the mass balance equation presented in (Ilaboya et al., 2013) as follows.

$$q = \frac{v}{m}\left[C_0 - C_e\right] \quad (1)$$

Where: q, defines the metal uptake (mg/g); C_0 and C_e: are the initial and equilibrium metal ion concentrations in the aqueous solution [mg/L] respectively; V: is the aqueous sample volume (mL) and m: is the mass of adsorbent used (g). The efficiency of metal ion removal (%) was calculated using the mass balance equation of the form (Badmus et al., 2007).

$$\text{Efficiency (\%)} = \left(\frac{C_0 - C_e}{C_0} \times 100\right) \quad (2)$$

Where: C_0 and C_e are the metal ion concentrations (mg/L) in aqueous solution before and equilibrium adsorption.

2.6 Design of experiment and process optimization

For Mn^{2+} ion adsorption, varied initial metal ion concentration of 4 – 20 mg/L, varied adsorbent dose of 0.2 – 1.0 g, varied pH of 2 – 10 and varied contact time of 24 – 120 mins for a constant adsorption temperature of 27 ± 2^0C were selected. The range and levels of the selected input variables is presented in Table 3

Table 3: Range and Levels of independent variables for Mn^{2+} ion adsorption

Independent Variables	Range and Levels				
	-2	-1	0	+1	+2
Initial metal ion concentration (mg/l)	4	8	12	16	20
pH	2	4	6	8	10
Adsorbent dose (g/L)	0.2	0.4	0.6	0.8	1.0
Contact time (minutes)	24	48	72	96	120

Using the parameters presented in Table 3, a full factorial central composite design comprising of sixteen factorial points, eight axial points and six replicates at the center point resulting in a total of 30 experimental runs as shown in Table 4 was employed to optimize the selected variables.

Table 4: Central composite design showing coded and real variables with observed and predicted Mn^{2+} ion adsorption

Experimental Runs	Coded Values of Variables				Real Values of Variables				Mn(II) Sorption Efficiency (%)	
	X_1 (mg/L)	X_2 (g/L)	X_3 (pH)	X_4 (mins)	X_1 (mg/L)	X_2 (g/L)	X_3 (pH)	X_4 (mins)	Observed	RSM Predicted
1	0	0	0	0	12.00	0.600	6.000	72.000	76.5	76.36
2	0	0	0	0	12.00	0.600	6.000	72.000	76.4	76.36
3	0	0	0	0	12.00	0.600	6.000	72.000	76.4	76.36
4	0	0	0	0	12.00	0.600	6.000	72.000	76.5	76.36
5	0	0	0	0	12.00	0.600	6.000	72.000	76.3	74.93
6	0	0	0	0	12.00	0.600	6.000	72.000	76.4	74.93
7	0	-2	0	0	12.00	0.200	6.000	72.000	75.8	74.80
8	0	+1	0	0	12.00	0.800	6.000	72.000	64.3	65.71
9	0	0	+1	0	12.00	0.600	8.000	72.000	74.3	73.41
10	0	0	-2	0	12.00	0.600	2.000	72.000	75.3	76.60
11	0	0	0	+1	12.00	0.600	6.000	96.000	65.2	64.48
12	0	0	0	-2	12.00	0.600	6.000	24.000	66.7	67.83
13	-1	0	0	0	8.000	0.600	6.000	72.000	67.1	63.33
14	-2	0	0	0	4.000	0.600	6.000	72.000	83.7	87.88
15	+2	+2	-2	+2	20.00	1.000	2.000	120.00	65.4	66.58
16	+2	+2	-2	-2	20.00	1.000	2.000	24.000	63.2	65.22
17	-2	-2	+2	-2	4.000	0.200	10.00	24.000	67.5	66.31
18	+2	-2	+2	+2	20.00	0.200	10.00	120.00	64.5	66.98
19	+2	-2	-2	-2	20.00	0.200	2.000	24.000	71.2	73.34
20	-2	+2	-2	+2	4.000	1.000	2.000	120.00	65.4	64.71
21	-2	-2	+2	+2	4.000	0.200	10.00	120.00	67.3	69.95
22	+2	+2	+2	-2	20.00	1.000	10.00	24.000	64.8	63.34
23	-2	+2	+2	-2	4.000	1.000	10.00	24.000	76.8	76.89
24	-2	-2	-2	-2	4.000	0.200	2.000	24.000	76.1	74.41
25	-2	+2	-2	-2	4.000	1.000	2.000	24.000	79.8	81.45
26	+2	+2	+2	+2	20.00	1.000	10.00	120.00	84.5	80.99
27	+2	-2	-2	+2	20.00	0.200	2.000	120.00	85.4	83.88
28	+2	-2	+2	-2	20.00	0.200	10.00	24.000	74.3	74.12
29	-2	-2	-2	+2	4.000	0.200	2.000	120.00	88.7	85.31
30	-2	+2	+2	+2	4.000	1.000	10.00	120.00	77.8	77.58

The behaviour of the system which was used to evaluate the relationship between the response variable (y) and the selected independent variables, namely; initial metal ion concentration (X_1), adsorbent dose (X_2), pH (X_3) and contact time (X_4) was explained using the empirical second-order polynomial equation of the form

$$Y = \beta_0 + \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \beta_{ii} x_i^2 + \sum_{i=1,i<j}^{q-1} \sum_{j=2}^{q} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

Where;
$X_1, X_2, X_3 \ldots X_k$ are the input variables;
Y is the response variable;
β_0, β_i, β_{ii}, and β_{ij}, (i = 1–k, j = 1–k) are the known parameters; and
ε is the random error.

To assess the model significance and justify the suitability of response surface methodology in optimizing the adsorption variables, one-way analysis of variance (ANOVA) was employed. To validate the ANOVA result, Fisher's F probability value and the probability function ($P < 0.05$) were employed. Large value of F corresponding to very low value of P ($P<<<0.05$) indicates the level of significance of the response surface model. To assess the reliability of the resulting second order polynomial equation, selected goodness of fit statistics, namely; coefficient of determination (R^2), adjusted (R-squared) value, predicted (R-squared) value and adequate precision value were employed. Adequate precision measures the signal to noise ratio while the reasonable agreement between the adjusted R-square and the predicted R-square measures the reliability of the optimal equation.

3. Results and Discussions

Scanning electron micrograph was taken in order to verify the presence of micropores. Scanning electron micrograph of raw and activated sawdust is presented in Figures 1a and 1b.

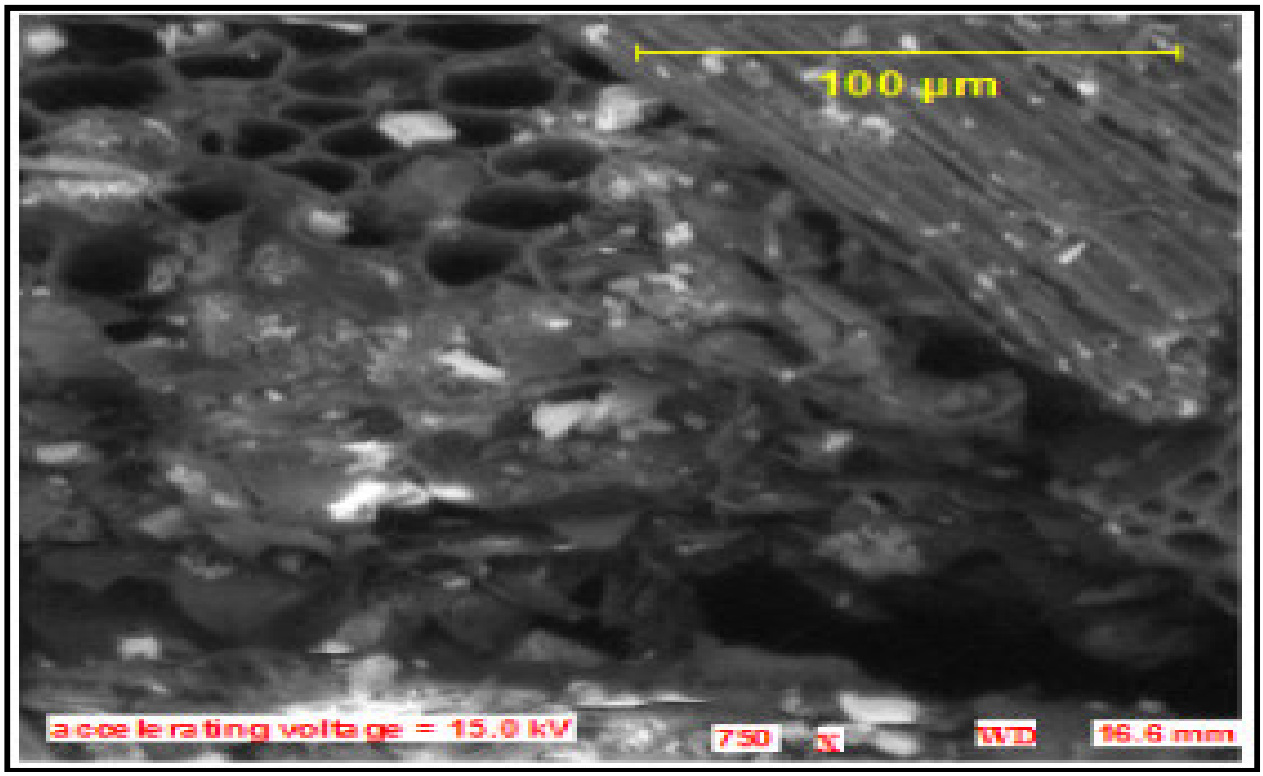

Figure 1a: Scanning electron micrograph of raw sawdust

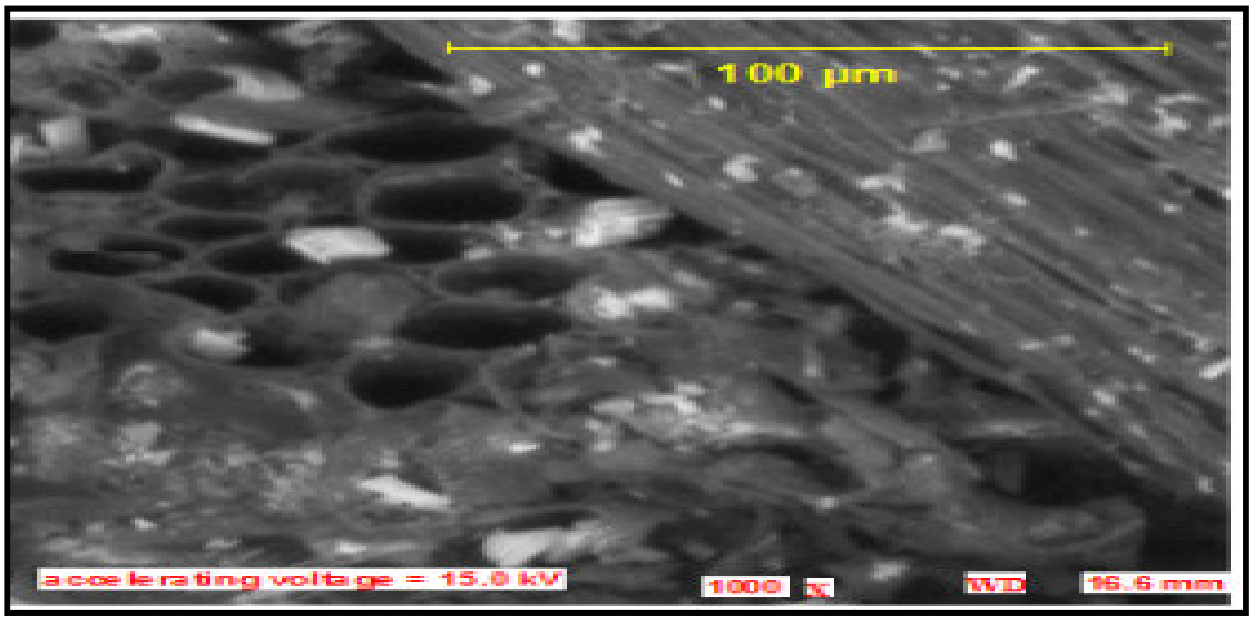

Figure 1b: Scanning electron micrograph of activated sawdust

Larger number of microporous structures observed with activated sawdust indicate a higher surface area hence better adsorption property. This claim is based on the fact that as biosorbent materials present larger numbers of microporous structure, they adsorb higher amount of nitrogen, which resulted to higher surface area and higher adsorption properties. Insight into the nature of functional groups that make up the surface of adsorbent would create a better picture on the adsorption potentials of the material. To identify the functional group's present on the surface of sawdust, Fourier Transform Infrared (FTIR) spectroscopy was used. Figure 2 shows the Fourier Transform Infrared (FTIR) spectra of raw sawdust.

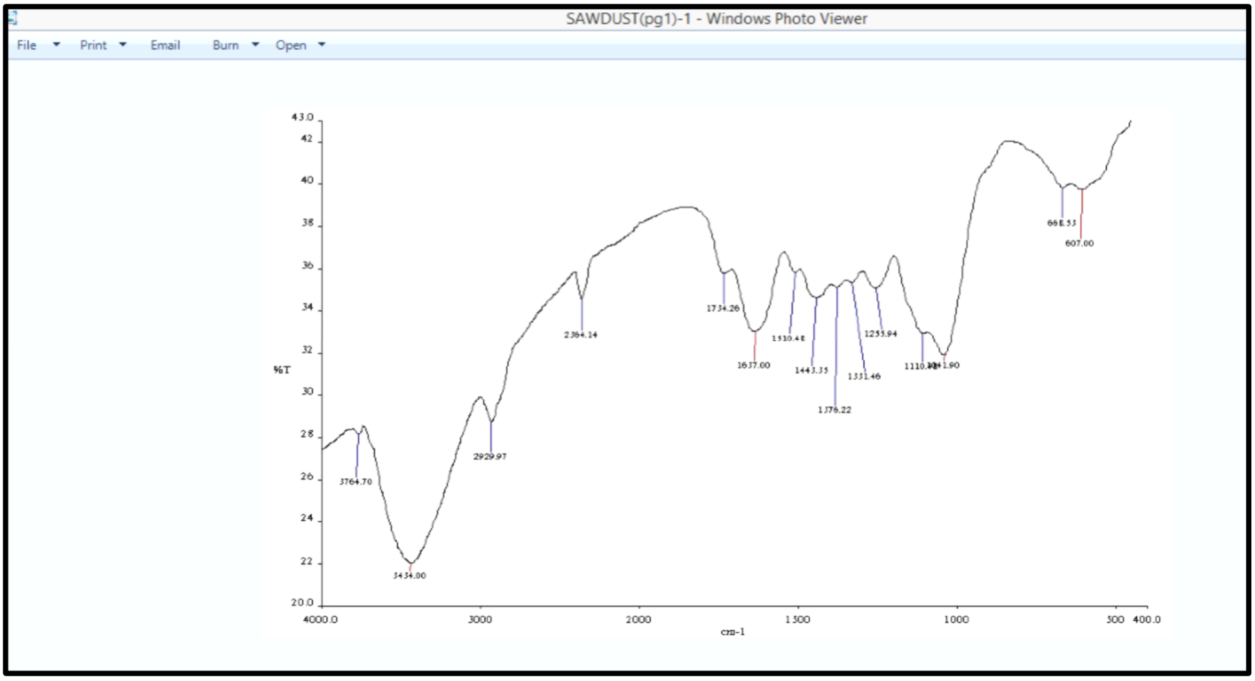

Figure 2: FTIR spectra of raw sawdust

To identify the functional group based on the FTIR spectra, absorption assigned bands from the work of previous researchers was employed to analyzed the spectrum of raw sawdust and result obtained is presented in Table 5

Table 5: Interpretation of FTIR spectrum of raw sawdust

S/No	Wave Number (cm^{-1})	Bond Source
1	3434.00	O-H stretching mode of hydroxyl groups N-H stretch
2	1637.00	N-H bending of amides, C ☰O stretch, carbonyl
3	1510.42	Quinonic and carboxylate groups, N-H bending, C ☰O stretch
4	1445.55	CH_2 and CH_2 bend, pyrones and aromatic group
5	1376.22	Organic phosphate, (P ☰O stretch)
6	1110.24	Organic siloxane or silicone, Si-O-C stretch
7	661.58	Disulphides (C - S stretch)

Result of Table 5 revealed that O-H stretching of hydroxide group and N-H stretching of amides are responsible for Mn^{2+} ion absorption onto zinc chloride activated sawdust. When the effect of varied adsorbent dose was studied at constant initial Mn^{2+} ion concentration of 20mg/L, optimum pH of 7.0, adsorption contact time of 120 minutes under a constant stirring speed of 150 rpm, result obtained is presented in Table 6

Table 6: Effects of adsorbent dose on the sorption of Mn^{2+} ion onto activated sawdust

S/No	Mass of Adsorbent (g)	C_0 (mg/L)	C_e (mg/L)	$C_0 - C_e$ (mg/L)	q (mg/g)	Efficiency (%)
1	0.2	20	16.55	3.450	172.5	17.25
2	0.4	20	12.77	7.230	361.5	36.15
3	0.6	20	9.87	10.13	506.5	50.65
4	0.8	20	6.45	13.55	677.5	67.75
5	1.0	20	5.72	14.28	714.0	71.40
6	1.2	20	3.77	14.28	714.0	71.40

Results of Table 6 revealed that adsorption efficiency increases with increasing dose of adsorbent reaching a maximum efficiency of 71.40 %. Higher dose of adsorbent will increase adsorption efficiency due to more active site and functional groups on the adsorbent surface which the metal could interact with. These chemical groups are important in the formation of van der Waal bonding since they played a major role in binding metals to adsorbents during adsorption process. To optimized the sorption variables and determine the maximum adsorption efficiency, response surface methodology using the quadratic polynomial model was employed. To validate the suitability of the quadratic model in analyzing the experimental data, the sequential model sum of squares was calculated and presented in Table 7

Table 7: Sequential model sum of square for sorption efficiency of Mn^{2+}

Response: Mn (II) Sorption						
*** WARNING: The Cubic Model is Aliased! ***						
Sequential Model Sum of Squares [Type I]						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Mean vs Total	161157.3813	1	161157.3813			
Block vs Mean	21.72016667	1	21.72016667			
Linear vs Block	1115.398333	4	278.8495833	14.05904722	< 0.0001	
2FI vs Linear	77.31375	6	12.885625	0.58173443	0.7403	
Quadratic vs 2FI	324.04075	4	81.0101875	15.18961359	< 0.0001	Suggested
Cubic vs Quadratic	38.70666667	8	4.838333333	0.807308323	0.6211	Aliased
Residual	35.959	6	5.993166667			
Total	162770.52	30	5425.684			
Sequential Model Sum of Squares [Type I]: Select the highest order polynomial where the additional terms are significant and the model is not aliased						

The sequential model sum of square shows the accumulating improvement in the model fit as terms are added. Based on the calculated sequential model sum of square, the highest order polynomial where the additional terms are significant and the model is not aliased was selected as the best fit. From the results of Table 7, it was observed that the cubic polynomial was aliased hence cannot be employed to fit the final model. In addition, the quadratic and factorial (2FI) models were suggesed as the best fit thus justifying the use of quadratic polynomial. The model statistics computed for the response variable based on the different model sources is presented in Table 8

Table 8: Model summary statistics for sorption Mn^{2+}

Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	4.45355741	0.7008831	0.65103028	0.55781557	703.700481	
2FI	4.70641652	0.74946476	0.61027851	0.48028554	827.083205	
Quadratic	2.30938561	0.95308232	0.90616464	0.79976054	318.664774	Suggested
Cubic	2.4480945	0.97740444	0.89455403	0.41499347	930.990209	Aliased
Model Summary Statistics: Focus on the model maximizing the "Adjusted R-Squared" and the “Predicted R-Square						

The summary statistics of model fit shows the standard deviation, coefficient of determination (r^2), adjusted r-squared, predicted r-squared and the predicted error sum of square (PRESS) statistic for each of the selected model. Low standard deviation, R-Squared near 1 and relatively low PRESS are the optimum criteria for selecting the best model for final optimization. Based on the results of Table 8, the quadratic polynomial model was suggested while the cubic polynomial model was aliased hence. Quadratic polynomial model posseses the highest adjusted r-square value of 0.90616464, highest predicted r-square value of 0.7997605 and lowest predicted error sum of square value of 318.664774. Analysis of the model standard error was employed to assess the suitability of response surface methodology using the quadratic model to maximize the sorption of Mn^{2+} onto sawdust. The computed standard error is presented in Table 9

Table 9: Result of computed standard errors

				Power at 5 % alpha level for effect of		
Term	**StdErr****					
Day 1	**0.193649**	**VIF**	**Ri-Squared**	**0.5 Std. Dev.**	**1 Std. Dev.**	**2 Std. Dev.**
A	0.204124	1	0	20.8 %	62.5 %	99.5 %
B	0.204124	1	0	20.8 %	62.5 %	99.5 %
C	0.204124	1	0	20.8 %	62.5 %	99.5 %
D	0.204124	1	0	20.8 %	62.5 %	99.5 %
AB	0.25	1	0	15.4 %	46.1 %	96.0 %
AC	0.25	1	0	15.4 %	46.1 %	96.0 %
AD	0.25	1	0	15.4 %	46.1 %	96.0 %
BC	0.25	1	0	15.4 %	46.1 %	96.0 %
BD	0.25	1	0	15.4 %	46.1 %	96.0 %
CD	0.25	1	0	15.4 %	46.1 %	96.0 %
A^2	0.190941	1.05	0.04761905	68.3 %	99.8 %	99.9 %
B^2	0.190941	1.05	0.04761905	68.3 %	99.8 %	99.9 %
C^2	0.190941	1.05	0.04761905	68.3 %	99.8 %	99.9 %
D^2	0.190941	1.05	0.04761905	68.3 %	99.8 %	99.9 %

**Basis Std. Dev. = 1.0

From the results of Table 9, it was observed that the model possesses a low standard error ranging from 0.204124 for the individual terms, 0.25 for the combined effects and 0.190941 for the quadratic terms. The computed error values were also observed to be less than the model basic standard deviation of 1.0 which suggests that response surface methodology was ideal for the optimization process. Variance inflation factor (VIF) of approximately 1.0 as observed in Table 9 was good since ideal VIF is 1.0. VIF's above 10 are cause for alarm, indicating coefficients are poorly estimated due to multicollinearity. Ri-squared value was observed to be between 0.0000 to 0.04761905 which is good. High Ri-squared (above 1.0) means that design terms are correlated with each other, possibly leading to poor model. Analysis of variance (ANOVA) was needed to check whether or not the model is significant and also to evaluate the significant contributions of each individual variable. Analysis of variance result is presented in Table 10

Table 10: ANOVA table for validating the model significance towards maximizing the sorption of Mn^{2+}

ANOVA for Response Surface Quadratic Model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Block	21.72016667	1	21.72016667			
Model	1516.752833	14	108.3394881	20.31392608	< 0.0001	**significant**
A-Initial metal ion conc.	86.26041667	1	86.26041667	16.17404474	0.0013	
B-Adsorbent dose	6.100416667	1	6.100416667	1.143843444	0.3029	
C-pH	5.13375	1	5.13375	0.962591017	0.3432	
D-Contact time	1017.90375	1	1017.90375	190.8595093	< 0.0001	
AB	18.275625	1	18.275625	3.426725581	0.0854	
AC	20.475625	1	20.475625	3.839231106	0.0703	
AD	1.265625	1	1.265625	0.237307866	0.6337	
BC	28.890625	1	28.890625	5.417064737	0.0355	
BD	4.305625	1	4.305625	0.8073155	0.3841	
CD	4.100625	1	4.100625	0.768877485	0.3954	
A^2	92.92526786	1	92.92526786	17.42372108	0.0009	
B^2	4.457410714	1	4.457410714	0.835775702	0.3761	
C^2	225.238125	1	225.238125	42.23271405	< 0.0001	
D^2	84.30026786	1	84.30026786	15.80651192	0.0014	
Residual	74.66566667	14	5.333261905			
Lack of Fit	40.57066667	10	4.057066667	0.475972039	0.8445	not significant
Pure Error	34.095	4	8.52375			
Cor Total	1613.138667	29				

The Model F-value of 20.31 as observed in Table 10 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, D, BC, A^2, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Lack of Fit F-value" of 0.48 implies the lack of fit is not significant relative to the pure error. There is a 84.45% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good as it indicate that the model is significant. On the significant contribution of the variables towards the sorption of Mn^{2+} ion, it was observed from the result of Table 10 that; initial metal ion concentration and contact time had the lowest calculated p-value of 0.0013 and >0.0001. Based on the calculated p-value, contact time was acclaimed the variable with the highest significant contribution followed by initial metal ion concentration. The goodness of fit statistics used to validate the adequacy of the quadratic model is presented in Table 11.

Table 11: Goodness of fit statistics used to validate the significance of model

1. Std. Dev.	2.309386	**5. R-Squared**	0.953082318
2. Mean	73.29333	**6. Adj. R-Squared**	0.906164637
3. C.V. %	3.150881	**7. Pred. R-Squared**	0.799760545
4. PRESS	318.6648	**8. Adeq Precision**	15.44585338

It was observed from the result of Table 11 that the "Predicted R-Squared" value of 0.7998 is in reasonable agreement with the "Adj R-Squared" value of 0.9062. Adequate precision measures the signal to noise ratio. A ratio greater than 4 as observed in Table 11 is desirable. The computaed ratio of 15.446 shows an adequate signal. Diagnostics case statistics which shows the observed values of sorption efficiency against the RSM predicted values is presented in Table 12.

Table 12: Diagnostics case statistics of observed and predicted sorption efficiency

Diagnostics Case Statistics									
Standard Order	**Actual Value**	**Predicted Value**	**Residual**	**Leverage**	**Internally Studentized Residual**	**Externally Studentized Residual**	**Influence on Fitted Value DFFITS**	**Cook's Distance**	**Run Order**
1	65.4	65.82667	-0.42667	0.6	0.292120654	0.282356347	-0.345814487	0.008	15
2	63.2	61.5975	1.6025	0.6	1.097164095	1.105865293	1.354402846	0.112853	16
3	67.5	66.3475	1.1525	0.6	0.789068093	0.777858791	0.952678565	0.058371	17
4	64.5	66.39333	-1.89333	0.6	-1.2962854	1.331598275	-1.630868158	0.157533	18
5	71.2	72.71417	-1.51417	0.6	1.036685991	1.039678085	-1.273340403	0.100755	19
6	65.4	63.96	1.44	0.6	0.985907206	0.984847663	1.206187125	0.091126	20
7	67.3	67.86	-0.56	0.6	0.383408358	0.371416647	-0.454890634	0.013781	21
8	64.8	63.38083	1.419167	0.6	0.971643502	0.969560851	1.187464679	0.088509	22
9	76.8	78.26417	-1.46417	0.6	1.002453102	1.002642551	-1.227981322	0.094211	23
10	76.1	75.16	0.94	0.6	0.643578315	0.629550189	0.771038365	0.038831	24
11	79.8	80.86	-1.06	0.6	0.725737249	-0.71287603	-0.873091262	0.049378	25
12	83.5	82.03083	1.469167	0.6	1.005876391	1.006332724	1.232500842	0.094855	26
13	85.4	83.12667	2.273333	0.6	1.556455357	1.649308697	* 2.02	0.227114	27
14	74.3	75.4975	-1.1975	0.6	0.819877694	0.809732376	-0.991715574	0.063019	28
15	78.7	80.3475	-1.6475	0.6	1.127973695	1.139977038	-1.396181031	0.11928	29
16	77.8	76.99333	0.806667	0.6	0.552290611	0.538094698	0.659028722	0.028596	30
17	79.9	79.385	0.515	0.183333	0.246767726	0.238310171	0.112912203	0.000854	1
18	78.2	79.385	-1.185	0.183333	0.567805349	0.553561979	-0.262279626	0.004524	2
19	76.4	79.385	-2.985	0.183333	1.430294488	1.491543194	-0.706698447	0.028703	3
20	81.7	79.385	2.315	0.183333	1.109256864	1.119221432	0.530291078	0.017264	4

Diagnostic case statistics actually give insight into the model strength and the adequacy of the optimal second order polynomial equation. Lower residual values resulting to higher leverages as observed in Table 12 is an indicator of a well fitted model. To asses the accuracy of prediction and established the suitability of response surface methodology using the quadratic model, a reliability plot of observed versus predicted sorption efficiency was generated and presented in Figure 3

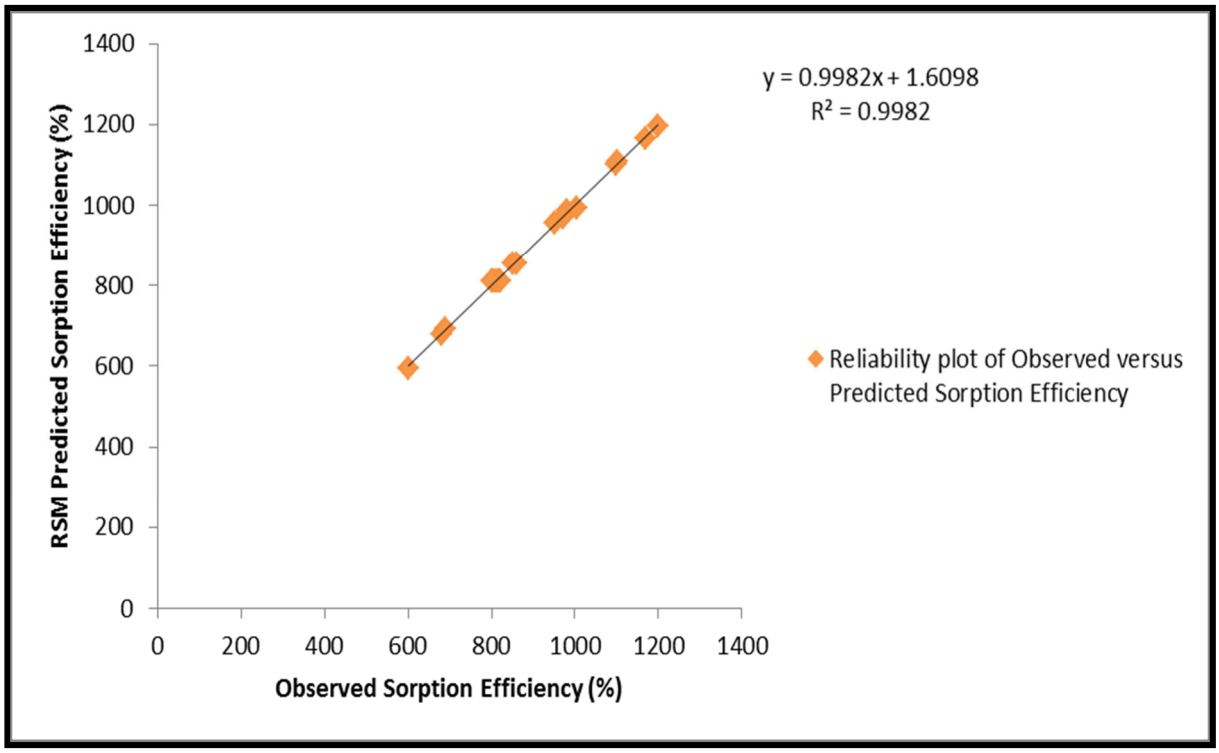

Figure 3: Reliability plot of observed versus predicted sorption efficiency

The high coefficient of determination (r^2 = 0.9982) as observed in Figures 3 was used to established the suitability of response surface methodology in maximizing the sorption efficiency. To accept any model, its satisfactoriness must first be checked by an appropriate statistical analysis output. To diagnose the statistical properties of the response surface model, the normal probability plot of residual presented in Figure 4 was employed.

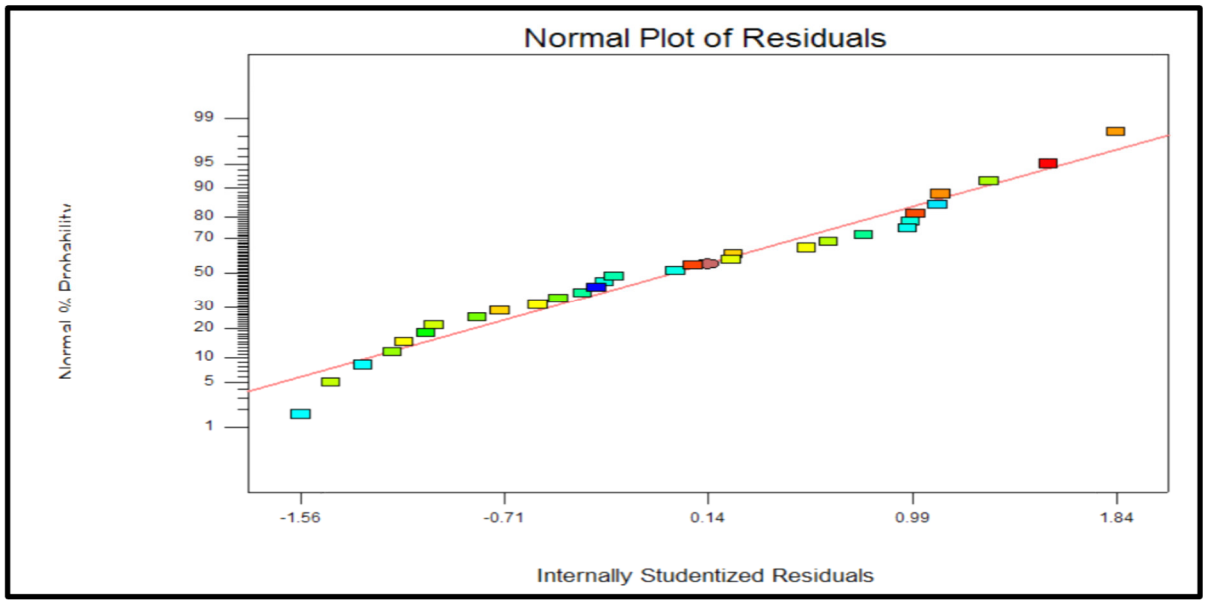

Figure 4: Normal probability plot of studentized residuals

The normal probability plot of residuals which is the number of standard deviations of actual values based on the predicted values was employed to ascertain if the residuals (observed – predicted) follows a normal distribution. It is the most significant assumption for checking the sufficiency of a statistical model. Results of Figures 4 revealed that the computed residuals are approximately normally distributed an indication that the model developed is satisfactory. To determine the presence of possible outliers, the cook's distance plot was generated. Cook distance is a measure of how much the regression would change if the outlier is omitted from the analysis. A point that has a very high distance value relative to the other points may be an outlier and should be investigated. The generated cook's distance plot is presented in Figure 5

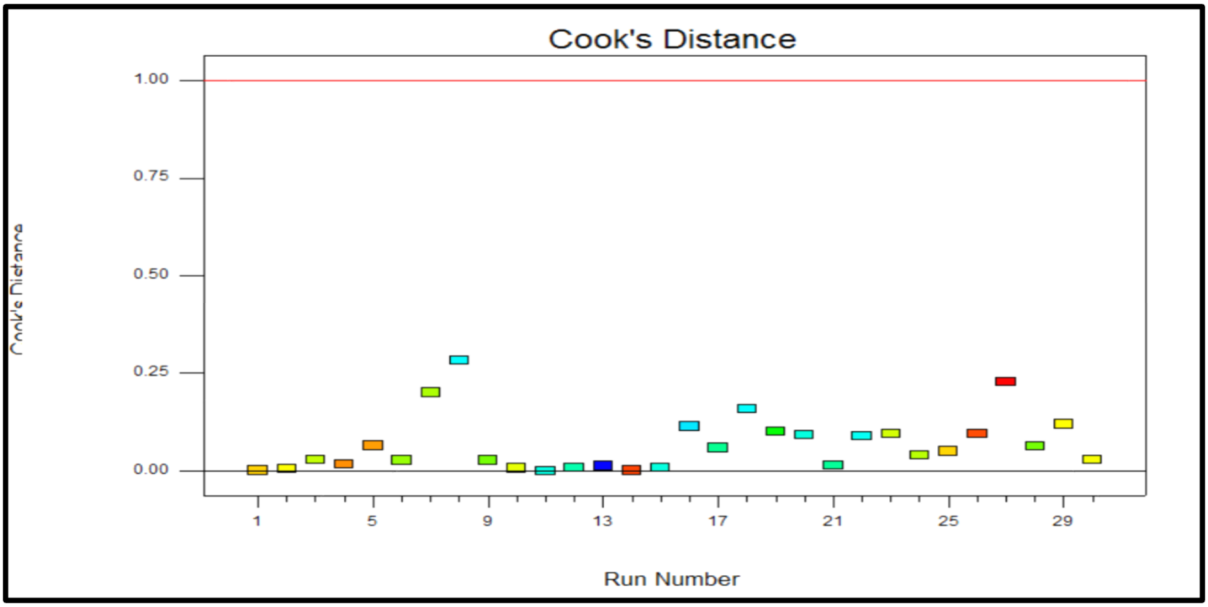

Figure 5: Generated cook's distance for the sorption of Mn^{2+} ion

The cook's distance plot has an upper bound of 1.00 and a lower bound of 0.00. The fact that all the experimental data are sandwich between the lower and the upper boundary as observed in Figure 5 is an indication that the data used for this analysis are devoid of possible outliers. To study the effects of combine input variables on the response variable (sorption efficiency), 3D surface plot presented in Figure 6 was employed.

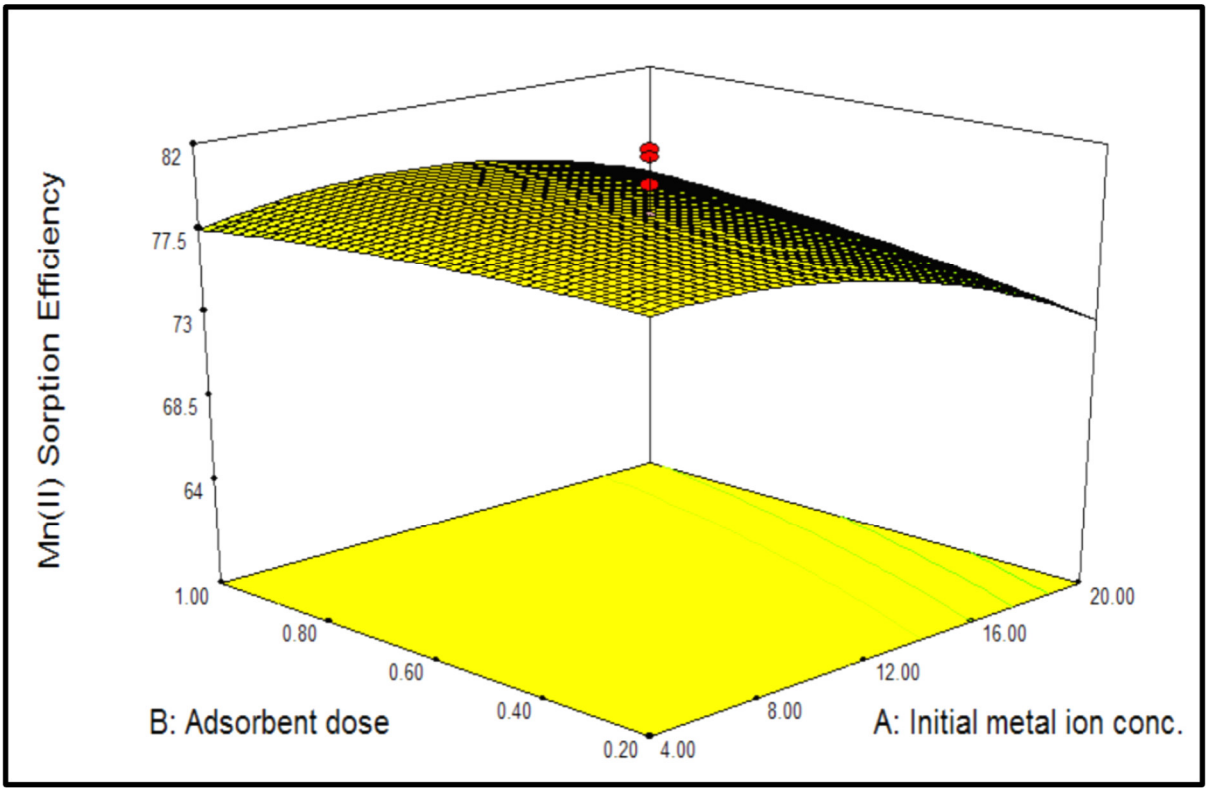

Figure 6: Effect of adsorbent dose and metal ion concentration on sorption of Mn^{2+} ion

Figure 6 shows the relationship between the input variables (adsorbent dose and initial metal ion concentration) and the response variable (sorption efficiency). It is a 3-dimensional surface plot which was employed to give a clearer concept of the response surface. Although not as useful as the contour plot for establishing response values and coordinates, this view provided a clearer picture of the interactions between the input and the response variable. A closer look at Figure 6 shows the presence of a coloured hole at the middle of the upper surface. That was a clue that more points lightly shaded for easier identification fell below the surface. From the surface plot of Figure 6, it was observed that the colour of the surface get darker towards initial metal

ion concentration and indication that this variable strongly influenced the adsorption Mn^{2+} ion.

Finally, numerical optimization was performed to ascertain the desirability of the model and determine the optimum dose of adsorbent, contact time, pH and initial metal ion concentration required to maximize the sorption of Mn^{2+} ion onto zinc chloride activated sawdust. The interphase of the optimization model showing the objective function is presented in Figure 7

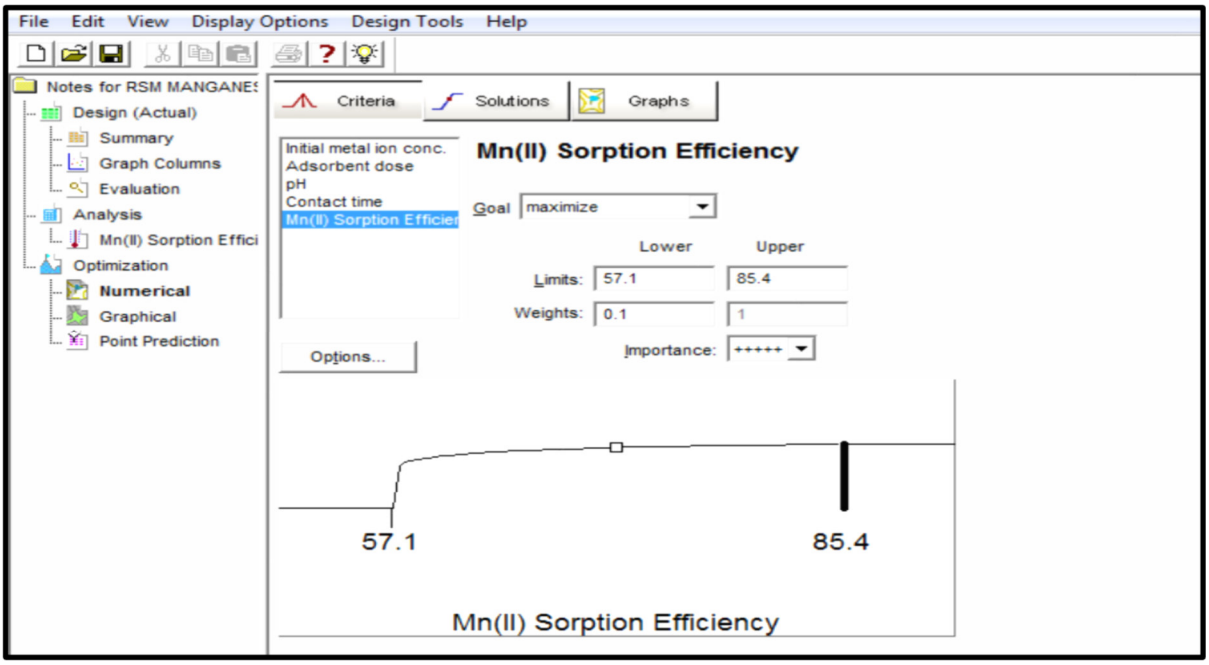

Figure 7: Interphase of numerical optimization for maximizing the sorption of Mn^{2+} ion

The optimization objective was to maximize the sorption efficiency. The relative importance was set at the optimum value of 5.0 and the lower and upper boundary conditions were set at 0.1 and 1.0 respectively. An upper boundary of 1.0 constraints the optimization tool to maximize the response variable. The final solution of numerical optimization is presented in Table 13

Table 13: Optimal solution of numerical optimization

Solutions							
Number	Initial metal ion conc.	Adsorbent dose	pH	Contact time	Sorption Efficiency	Desirability	
1	11.33	1	5.13	120	84.03945858	0.995085145	Selected
2	11.44	1	5.1	120	84.03944263	0.995085086	
3	11.39	1	5.15	119.99	84.03915471	0.995084022	
4	11.22	1	5.1	119.96	84.03679818	0.995075317	
5	11.72	1	5.22	120	84.03211161	0.995058003	
6	11.41	1	5	119.92	84.03131388	0.995055056	
7	12.17	1	5.01	120	84.02253069	0.995022599	
8	11.4	1	4.7	119.99	84.012187	0.994984363	
9	10.66	0.98	5.3	120	84.0114497	0.994981637	
10	10.11	1	5.21	120	83.99750092	0.994930053	
11	10.83	0.96	5.11	120	83.99131687	0.994907176	
12	11.23	1	5.29	119.38	83.98750891	0.994893087	
13	11.58	1	4.76	119.17	83.95632931	0.994777656	
14	9.5	1	5.74	120	83.90758717	0.994596964	
15	11.15	1	5.22	118.3	83.90703742	0.994594924	
16	9.7	0.87	5.9	120	83.8676513	0.994448697	
17	10.83	1	5.07	116.64	83.77024173	0.994086215	

Based on the optimization results, the model equation which shows the relationship between the selected input variables and the response variable was developed as follows;

$$Mn^{2+}\,Sorption\ Efficiency = 52.16375 + 0.41224(conc.) + 3.36979(adsorbent\ dose) + 3.38281(pH)$$
$$+ 0.23607(contact\ time) + 0.33398(conc. \times \text{dose}) - 0.035352(\text{conc.} \times \text{pH}) + 7.32422\text{E} - 004(\text{conc.} \times \text{time})$$
$$- 0.83984(\text{adsorbent dose} \times \text{pH}) + 0.027018(\text{adsorbent dose} \times \text{contact time}) - 2.63672\text{E} - 003(\text{pH} \times \text{time})$$
$$- 0.028760(\text{conc})^2 - 2.51953(adsorbent\ \text{dose})^2 - 0.1710(pH)^2 - 7.60905E - 004(contact\ \text{time})^2$$

The optimal values of the input variables as observed in Table 13 are given as follows;

i. Initial metal ion concentration of 11.33 mg. which indicate 11.33 mg/L of manganese in 50ml aqueous solution
ii. Adsorbent dose of 1.0 g
iii. pH (5.13) which is assumed to be (5.0)
iv. Contact time (120 minutes)

Under this operating condition and using zinc chloride activated sawdust as adsorbent for the treatment of aqueous solution containing 11.33 mg/L of Mn^{2+} ion, 84.04 % removal efficiency was obtained. This solution was selected by design expert as the optimal solution with a desirability value of 99.51 %. Finally, based on the optimal solution, the contour plot showing the response variable against the optimized value of the input variables is presented in Figure 8. The contour plot can be employed to predict the optimum values of the input variables based on the flagged response variable.

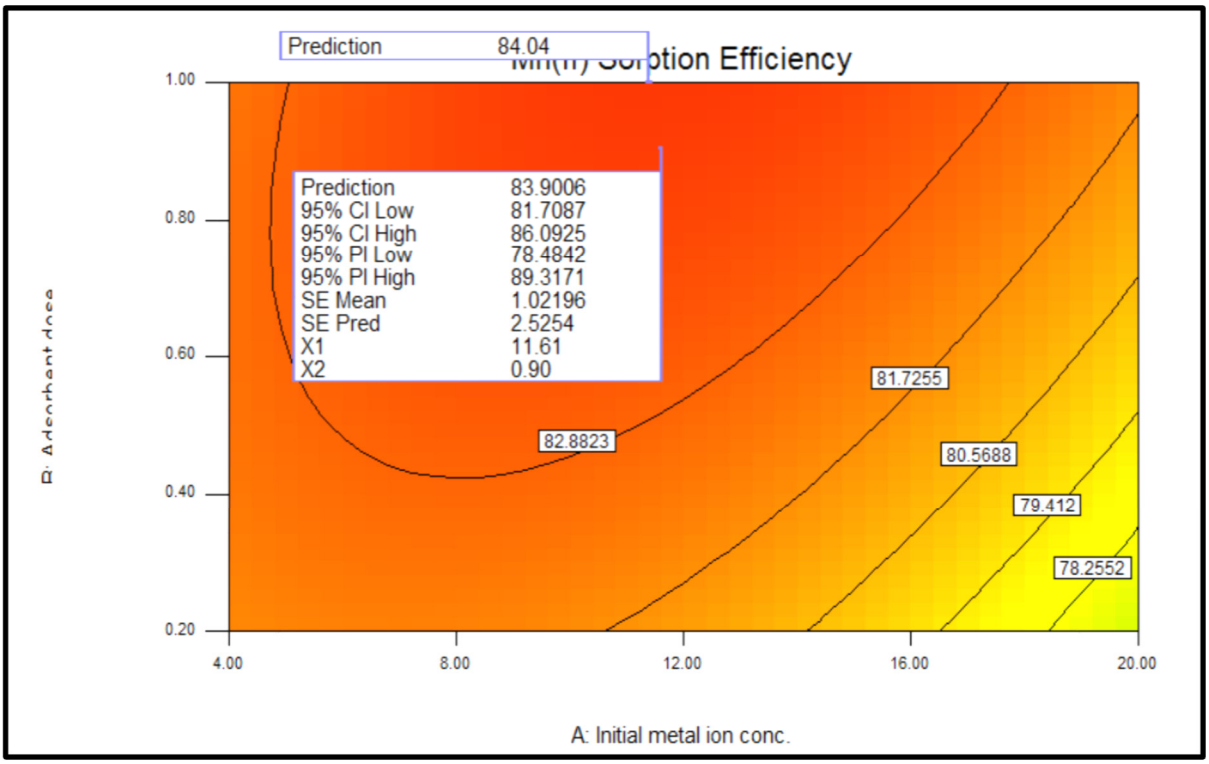

Figure 8: Predicting sorption of Mn^{2+} ion using contour plot

4. Conclusion

The potential of zinc chloride activated sawdust as adsorbent for the removal of manganese from aqueous solution has been studied. From the result, it was concluded that sawdust has the potential to remove divalent metals from water and wastewater. In addition, the performance of statistical design of experiment and response surface methodology in optimizing the sorption of divalent metal ion onto zinc chloride activated sawdust has been successfully implemented and will form the bases for future research in related areas. The optimal values of selected input variables, namely; adsorbent dose, pH, contact time and initial metal ion concentration that will yield a better sorption efficiency and ensure a more effective wastewater treatment has also been calculated withh the optimal equation clearly presented. Although, the study is not completely exhaustive of the subject matter, it has provided additional information to the existing literatures on modelling and optimization of metal ion absorption onto activated solid adsorbents

5.0 References

Badmus, M.A.O.; Audu T.O.K & Anyata, B.U, (2007), Removal of lead ion from industrial wastewaters by

activated carbon prepared from periwinkle shells, Turkish Journal of Engineering and Environmental Science, 251 – 263

Cerino-Cordova, F.J; Garcia-Leon, A.M; Garcia-Reyes, R.B; Garza-Gonzalez, M.T; Soto-Regalado, E; Sanchez-Gonzalez, M.N & Quezada-Lopez, I (2011), Response surface methodology for lead biosorption on Aspergillus Tesseus, International Journal of Environmental Science and Technology, vol. 8(4), 695-704

Dawodu, F.A.; Akpomie, G.K.; Ejikeme, M.E., & Ejikeme, P.C.N., (2012), The use of Ugwuoba clay as an adsorbent for zinc (II) ions removal from solution, International Journal of Multidisciplinary Science and Engineering, vol. 3(8), 13 – 18

Demirbas, E; Mehmet, K; Senturk, E & Tuncay, O (2004), Adsorption kinetics for the removal of chromium (VI) from aqueous solution on activated carbon prepared from agricultural wastes, Water SA, vol. 30(4), 533-539

Drinking Water Inspectorate, (2014); Guardians of drinking water quality; what are the drinking water standards? http//www.dwi.gov.uk

Ekpete, O.A. & Horsfall, M. JNR, (2011), Preparation and Characterization of Activated Carbon derived from Fluted Pumpkin Stem Waste, Research Journal of Chemical Sciences, Volume 1(3), 10 – 17

Ikenyiri, P.N., Abowei, F.M.N., Ukpaka, C.P & Amadi, S.A. (2019), Characterization and physico-chemical properties of wood sawdust in Nigeria area, Nigeria, Chemistry International, 5(3), 190-198

Ilaboya & Izinyon, (2019); Modeling and prediction of sorption of Pb (II) and Mn (II) ions from aqueous solution onto acid activated shale using statistical design of experiment (DOE) and modular neural network (MNN), Journal of Civil and Environmental Systems Engineering, vol. 17(1), 113-124

Ilaboya, I.R; Oti, E.O; Ekoh, E.O. & Umukoro, L.O. (2013); Performance of activated carbon from cassava peels for the treatment of effluent wastewater, Iranica Journal of Energy & Environment (IJEE), an Official Peer Reviewed Journal of Babol Noshirvani University of Technology, vol. 4 (4), 361-375.

Izinyon, O.C; Nwosu, O.E; Akhigbe, I.O., & Ilaboya, I.R., (2016), performance evaluation of Fe (III) adsorption onto brewer's spent grain, Nigerian Journal of Technology (NIJOTECH), vol. 35(4), 970 – 978

Jaikumar, V., & Ramamurthi, V., (2009), Statistical Analysis and Optimization of Acid Dye Biosorption by Brewery Waste Biomass Using Response Surface Methodology, Modern Applied Science, Vol. 3(4), 71 – 84

Khurshid, S.J and Qureshi, I.H., (1984); Role of Inorganic Elements in the Human Body, the Nucleus, 21, 3 – 23

Kumar, N.K; Reddy, D.S.R & Venkateswarlu, P (2010), Application of response surface methodology for optimization of chromium biosorption from aqueous solution onto Syzigium Cumini (Java) seed powder, Microbial and Biochemical Technology, vol. 2(1), 020-027

Mansfield, G.R., (1996), Clay Investigation in Southern States, US Geological Survey Bulletin 901, pp1-22

Mariadas, K.; Kalyani, G.; Joga, H.R.; Kumar, P. Y & King, P., (2012), The removal and equilibrium studies of cadmium by natural clay as adsorbent, International Journal of Scientific Engineering Research, Vol. 3(8), 1-6

Montgomery, D.C. (1996), Design and Analysis of Experiments, John Wiley & Sons, New York; 34 – 56

Omisanya, N.O.; Folayan, C.O.; Aku, S.Y & Adefila, S.S., (2012), Synthesis and characterization of zeolite for adsorption Refrigeration application, Advance in Applied Science Research, Vol. 3(6), 3746-3754

Sekar, M; Sakthi, V & Rengaraj, S., (2004), Kinetics' and equilibrium studies of lead (11) onto activated carbon prepared from coconut shell, Journal of Colloid and Interface Science, vol. 279, 307 – 313

Weng, C.H; Tsai, C.Z; Chu, S.H & Sharma, Y.C., (2007), Adsorption characteristics of copper (II) onto spent activated clay, Separation Purification Technology Journal, vol. 54, 187-197

Ziemacki, G; Viviano, G & Merli, F., (1989), Heavy metals; sources and environmental presence, Ann. 1st Super Sanita, vol. 25(3), 531 – 536

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