Research Article GU J Sci 35(2): 421-432 (2022) DOI: 10.35378/gujs.796618

Gazi University

Journal of Science

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Statistically Optimized Adsorption of Pb(II) Ion on Corn Husk Activated Carbon – An Application of Response Surface Method

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Highlights

- This paper focuses on Pb(II) adsorption on sorbent prepared from agricultural waste.
- A statistical approach is adopted for adsorption optimization.
- The method of optimization was quick and environmentally friendly.

Article Info

Received: 17 Sep 2020
Accepted: 02 June 2021

Keywords

Adsorption,
Corn Husk,
Activation optimization,
Response Surface Method,
Adsorption Isotherm

Abstract

In this study, the Response Surface Method statistically optimized Pb(II) adsorption on activated carbon prepared using corn husk. The full central composite design was the statistical method selected for optimization using adsorption capacity as a response factor. The quadratic model best explained the process. Adsorption parameters optimized were solution pH, contact time, temperature, and adsorbent dose. The respective optimum values were 4.5, 64 min, 50°C, and 0.4 g L^{-1}. Adsorption isotherm and kinetics studies evaluated the data obtained at different temperatures using different isotherm and kinetics models. The non-linear curve fitting method determined the model with the best fit. Freundlich's model best accommodated the isotherm data, whereas the pseudo-second-order kinetic model best modeled the kinetics data. Weber-Morris intraparticle diffusion model revealed the existence of multiple rate-controlling processes. The activation energy for the adsorption of Pb(II) ions was 30.17 kJ mol^{-1}. The thermodynamics studies showed that the process was an entropy-driven endothermic process. Gibb's free energy (ΔG) values were negative at the studied temperatures, and the spontaneity increased with the increase in temperature. The enthalpy (ΔH) and entropy change (ΔS) was 43.78 kJ mol^{-1} and 154.2 J mol K^{-1}. The study concluded that the statistical method simplified the optimization of the adsorption process and produced an efficient adsorbent from corn husk.

1. INTRODUCTION

Optimization of the adsorption process is a lengthy process, and it requires several trials to reach the optimum conditions. The presence of interaction among the variables further complicates the optimization. The statistical methods can simplify the optimization process and help us achieve the same or even better conclusion in relatively less time while consuming even fewer chemicals.

Several studies reported the preparation of activated carbon [1] and biosorbent [2] from corn husk. These studies mostly used methylene blue as the adsorbate. There are also studies reported for the biosorption of emulsified oil [3], phenols, and cyanides [4] on the sorbent. Based on the available literature review, there is a scarcity for the statistically optimized adsorption of metal ions on the corn husk adsorbent. Moreover, the optimization studies for the adsorptive removal of Pb(II) ions using activated carbon from corn husk are not reported yet.

This study focused on the efforts to statistically optimize Pb(II) adsorption on the activated carbon. The optimization studies based on the Response Surface Method (RSM) for the design of the experiment determined the optimum values for adsorption variables. The selected variables were solution pH, contact time, temperature, and the adsorbent dose. The central composite design (CCD) analyzed the interaction

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between the variables. The adsorption isotherm and kinetics studies provided data to obtain thermodynamic insight into the adsorption process.

2. EXPERIMENTAL

2.1. Statistical Optimization

The mode of adsorption selected for the optimization studies was the batch mode. Each run started with a transfer of a known amount of adsorbent to a beaker carrying a known volume of Pb(II) solution. The volume and concentration of the solution were 100 mL and 100 mg L^{-1} Pb, respectively. The adsorbent dose, adsorption time, pH, and temperature were set for each run, as shown in Table 1. The run ended with filtration of 10 mL aliquot using a 0.45μm cellulose acetate membrane filter. The technique used for the determination of Pb(II) was flame atomic absorption spectrophotometry.

2.2. Isotherm Studies

The general procedure used for adsorption isotherms studies was the same as mentioned in section 2.1. The amount of adsorbent was 0.04 g, and the run time was twelve hours to reach equilibration. A thermostated horizontal shaker maintained the temperature and agitated the solutions for isothermal studies. The shaking speed was 125 rpm. The range of initial Pb(II) concentration was 50 to 300 mg L^{-1}, and the temperature range was 298 to 313 K with an interval of 5K.

2.3. Kinetics Studies

The experimental for adsorption kinetics was the same as that used for isotherm studies, section 2.2, except that the initial Pb(II) concentration was 100 mg L^{-1}. The run-time range was 10 to 60 min.

2.4. Response Surface Method for Design of Experiment

In this study, the RSM was used to obtain optimum values of pH, temperature, adsorbent dose, and time for the adsorption of Pb(II) ions at corn husk activated carbon. Response Surface Method is a powerful statistical tool used to determine optimized conditions for a physical process. The optimization starts with the method suggested run table based on the provided limits for each variable. The next step is to determine the value of the response factor for each run. The method then performs regression analysis using various models and yields statistical parameters and residuals values for each model. The optimum model is selected based on the minimum values of residuals [5]. The method correlates the effect of variables on the response factor using a polynomial expression as follows

$$\mathrm{Y} = x_0 + x_1\mathrm{X} + x_2\mathrm{Y} + x_3\mathrm{Z} + x_{12}\mathrm{XY} + x_{23}\mathrm{YZ} + x_{31}\mathrm{ZX} + x_{11}\mathrm{X}^2 + x_{22}\mathrm{Y}^2 + x_{33}\mathrm{Z}^2 + \cdots.$$

Independent variables like time, temperature, and pH, are symbolized as X, Y, and Z. The response factor, adsorption capacity, is Y. The linear coefficients for the independent variables are $x_1, x_2,$ and x_3. The coefficients for two-factor interactions are x_{12}, $x_{23}, and\ x_{31}$. The quadratic coefficients for the independent variable are x_{11}, x_{22}, and x_{33} and x_0 is the intercept. The software used to process the RSM method was Design-Expert software (version 10.0.4.0, Stat Ease Inc., USA).

3. RESULTS AND DISCUSSION

3.1. Adsorbent Characterization

The characterization study of corn husk activated carbon comprises an evaluation of the surface functional groups using IR spectroscopy and porosity analysis using SEM images.

Fourier Transform Infrared Study

Figure 1 shows FTIR Spectra of corn husk sorbent. A broad peak observed for the wavenumbers 3000 – 3652 cm^{-1} corresponds to N – H or O – H groups stretching. The presence of – OH indicates the existence of phenolic or carboxylic groups at the surface. Stretching of single-bonded hydrocarbon (methyl or methylene) was observed at 2864 – 2924 cm^{-1}. However, the band at 1550 – 1654 cm^{-1} corresponds to the presence of C=O or C=C stretching. A strong peak in 1100 – 1300 cm^{-1} indicates the presence of sulfonate (C-S-O) and phosphate (P-O-C asymmetric stretch). Weak peaks observed for corn husk activated carbon in the range of 1000 – 1400 cm^{-1} predicted the presence of sulfur-containing groups, which might have developed upon treatment of the substrate with sulfuric acid in the activation process.

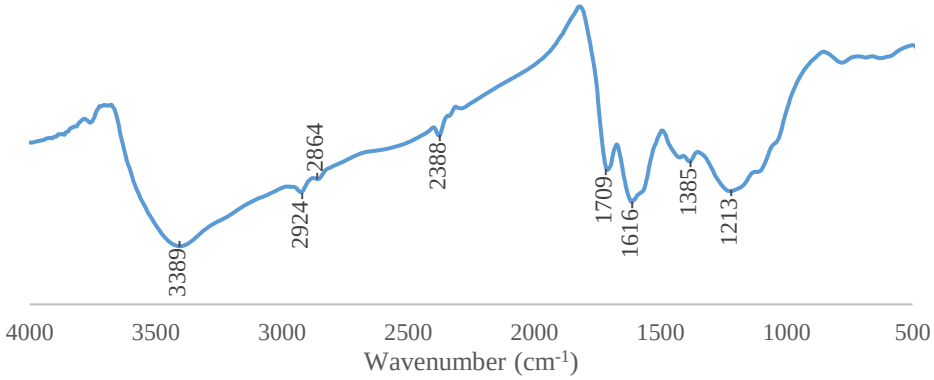


Figure 1*. FT IR spectrum of corn husk activated carbon*

Scanning Electron Microscopic Study

The adsorption process can remove the pollutants from the aqueous medium. However, its effectiveness depends much on the surface area of the adsorbent, which in turn depends upon its porosity. SEM images show the porosity at a glance. The image obtained at 10kV and ×1500 magnification revealed that the adsorbent was highly porous, and it had plenty of macropores at the surface, as shown in Figure 2.

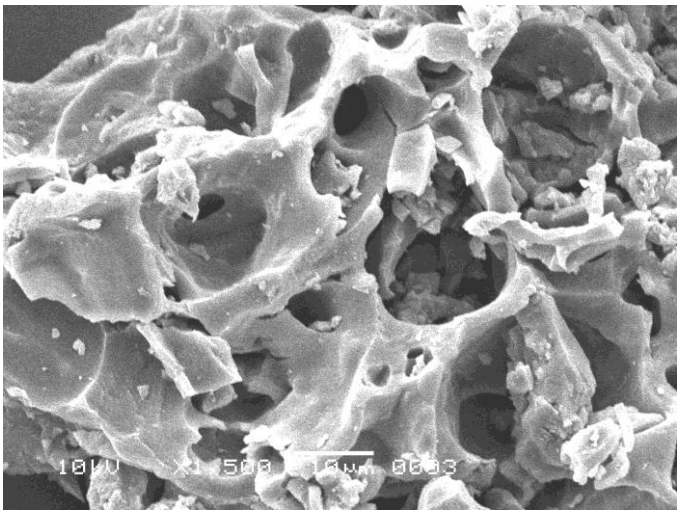


Figure 2*. SEM image of activated carbon prepared from corn husk*

3.2. Optimization of the Adsorption Process

The adsorption properties of activated carbon prepared from corn husk were studied using Pb(II) ions as the adsorbate. Adsorption process optimization was studied using Response Surface Method. Full Central Composite design comprising 30 randomized runs in two blocks optimized the response factor, i.e., the adsorption capacity. The experimental factors optimized were solution pH, contact time (min), solution

temperature (°C), and the adsorbent dose (g L^{-1}). Table 1 shows the design table and the corresponding values of adsorption capacity for each run.

Model Statistics

The statistical models used to fit in the adsorption data were Linear, 2 – factor interaction (2FI), Quadratic, and Cubic models. The standard deviation for quadratic and cubic models were 0.0062 and 0.0037, respectively, whereas the values for linear and 2FI models were 0.45 and 0.52. The model statistics suggested using cubic and quadratic models to further evaluate the adsorption data due to the small value of standard deviation. R – squared values followed the same trend as observed for standard deviation. Cubic and quadratic models had the highest value of 1.0 and 0.9999, whereas linear and 2FI models had lower values of 0.5387 and 0.5392, respectively [6]. The aliasing in the cubic model inhibited the further evaluation of the model. Therefore, the quadratic model turned out to be best for optimizing the adsorption parameters.

Table 1. *The Response Surface design table with corresponding values of response factor*

Block	Run	Space Type	W:pH	X:Time	Y:Temp	Z: Dose	Capacity
				min	°C	g L^{-1}	mg g^{-1}
1	1	Interior	3.5	44	35	0.5	44.6
1	2	Factorial	5.0	90	50	0.1	51.8
1	3	Factorial	5.0	05	20	0.1	2.3
1	4	Interior	3.5	44	35	0.5	43.9
1	5	Factorial	2.0	90	20	0.1	6.5
1	6	Interior	3.5	44	35	0.5	44.6
1	7	Factorial	5.0	05	50	0.8	4.0
1	8	Factorial	2.0	05	50	0.1	1.8
1	9	Factorial	2.0	05	20	0.1	0.7
1	10	Factorial	5.0	05	50	0.1	5.9
1	11	Factorial	2.0	90	50	0.1	15.8
1	12	Factorial	5.0	05	20	0.8	1.6
1	13	Factorial	2.0	05	20	0.8	0.5
1	14	Interior	3.5	44	35	0.5	44.0
1	15	Factorial	2.0	90	20	0.8	4.3
1	16	Factorial	5.0	90	20	0.1	21.2
1	17	Factorial	2.0	90	50	0.8	10.6
1	18	Factorial	2.0	05	50	0.8	1.2
1	19	Factorial	5.0	90	50	0.8	36.0
1	20	Factorial	5.0	90	20	0.8	14.6
2	21	Interior	3.5	44	35	0.5	44.5
2	22	Interior	3.5	44	35	0.5	44.4
2	23	Interior	3.5	44	35	1.0	6.0
2	24	Interior	1.0	44	35	0.5	1.8
2	25	Interior	3.5	136	35	0.5	17.0
2	26	Interior	3.5	44	5	0.5	14.2
2	27	Interior	3.5	05	35	0.5	7.5
2	28	Interior	5.0	44	35	0.5	37.3
2	29	Interior	3.5	44	35	0.1	28.0
2	30	Interior	3.5	44	65	0.5	88.1

Analysis of Variance (ANOVA)

The ANOVA for the response surface quadratic model evaluated the appropriateness of the model. The sum of squares, degree of freedom (df), mean squares (the variances), the F- values, and p – values for the terms used in the model development are in Table 2. The model defined the parameters pH, contact time,

solution temperature, and adsorbent dose as W, X, Y, and Z, respectively. ANOVA showed that W^2, X^2, Y^2, and Z^2 were the significant multiple-of-basic-terms with a p-value less than 0.05 [7]. The p-value obtained for the lack of fit was 0.0668 (>0.05), which showed that the lack of fit was insignificant compared to the pure error of the model.

Adequate precision is a measure of the signal-to-noise ratio. A value greater than 4.0 predicts an excellent signal-to-noise ratio. The adequate precision for the model was 595.3, which concluded an excellent signal-to-noise ratio for the model.

Equation (1) shows the mathematical relation comprising of the significant terms.

$$\mathrm{Log_{10}Capacity} = -2.710 + 1.243\mathrm{W} + 0.0288\mathrm{X} + 0.0208\mathrm{Y} + 2.007\mathrm{Z} - 0.1527\mathrm{W}^2 - 1.849 \times 10^{-4}\mathrm{X}^2 - 1.094 \times 10^{-4}\mathrm{Y}^2 - 2.494\mathrm{Z}^2 \quad (1)$$

Table 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	0.88	1	0.88			
Model	10.58	8	1.32	30640.10	< 0.0001	Significant Model Terms
W-pH	1.26	1	1.26	29078.17	< 0.0001	
X-Time	4.09	1	4.09	94852.44	< 0.0001	
Y-Temp	0.94	1	0.94	21687.62	< 0.0001	
Z- Dose	0.13	1	0.13	3019.78	< 0.0001	
W^2	1.11	1	1.11	25744.59	< 0.0001	
X^2	1.87	1	1.87	43386.71	< 0.0001	
Y^2	0.017	1	0.017	402.34	< 0.0001	
Z^2	0.77	1	0.77	17756.24	< 0.0001	
Residual	8.63×10^{-4}	20	4.32×10^{-5}			
Lack of Fit	8.22×10^{-4}	16	5.14×10^{-5}	4.94	0.0668	not significant
Pure Error	4.16×10^{-5}	4	1.04×10^{-5}			
Cor Total	11.46	29				

Diagnostics

The diagnostic tools further evaluated the model using externally studentized residuals. The residuals had a normal distribution as observed from the random scatter of residuals around the straight line in the normal plot. Figure 3 showed a megaphone pattern that concluded an expanding variance of the residuals and recommended the data transformation. The residual vs. run plot diagnosed the effect of time-related variables. Random scatter in the data confirmed the absence of time-based trends in the adsorption process. Box-Cox plot predicted the type of transformation applied to the data. The minimum observed at the lambda value 0 suggested a log transformation for the data.

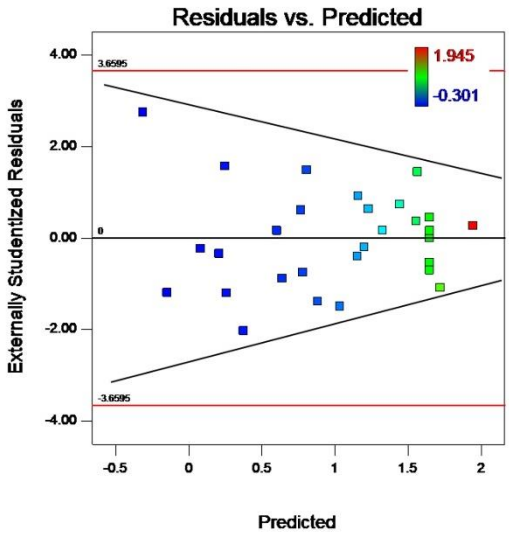
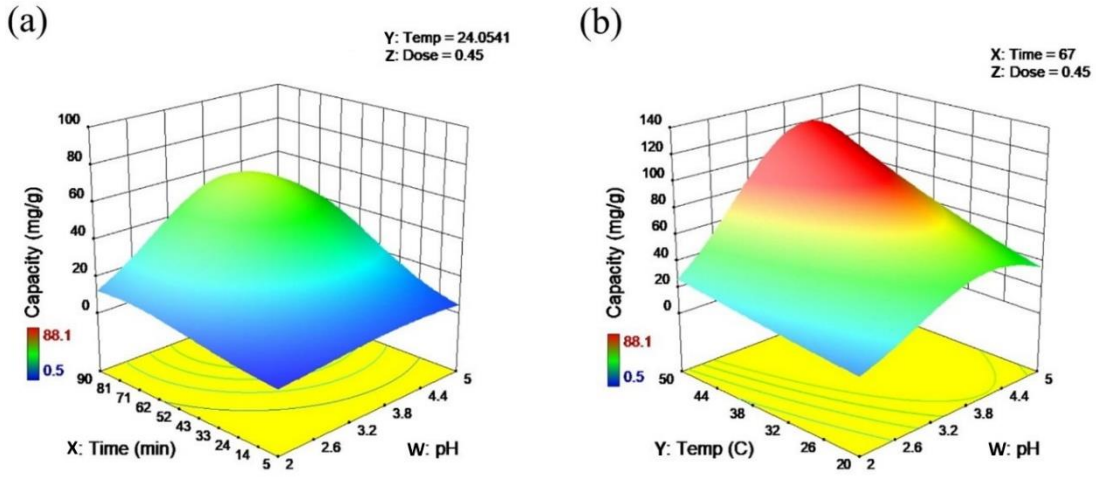


Figure 3*. Residuals versus Predicted Diagnosis Plot for Response Surface Quadratic Model for the optimization of the adsorption process*

Surface Plots

Figure 4 shows the 3D plots for the surface response quadratic model prepared by varying two factors while keeping the remaining two factors constant. Figure 4(a) shows that pH had a prominent effect on the adsorption capacity of adsorbent for Pb(II) ions. A maximum observed for the pH range 3.8 to 4.4. The effect of varying temperatures was linear, as observed in Figure 4(b). Increasing temperature from 20 °C to 50 °C resulted in a proportional increase in the adsorption capacity indicating the endothermic nature of the adsorption process. Figure 4(c) shows the effect of varying contact time on the adsorption capacity of activated carbon. An increase in contact time resulted in increased adsorption capacity, which even out after reaching a maximum value. The leveling effect shows that the system attains equilibrium after a specific time interval. Figure 4(d) shows the impact of varying adsorbent doses. The adsorption capacity was maximum in the dose range 0.4 to 0.5 g L^{-1}. The low value of adsorption capacity at doses lower than 0.4 g L^{-1} corresponds to the scarcity of adsorption sites in the system. The decrease in adsorption capacity at doses higher than 0.5 g L^{-1} corresponds to the shortage of adsorbate in the system.



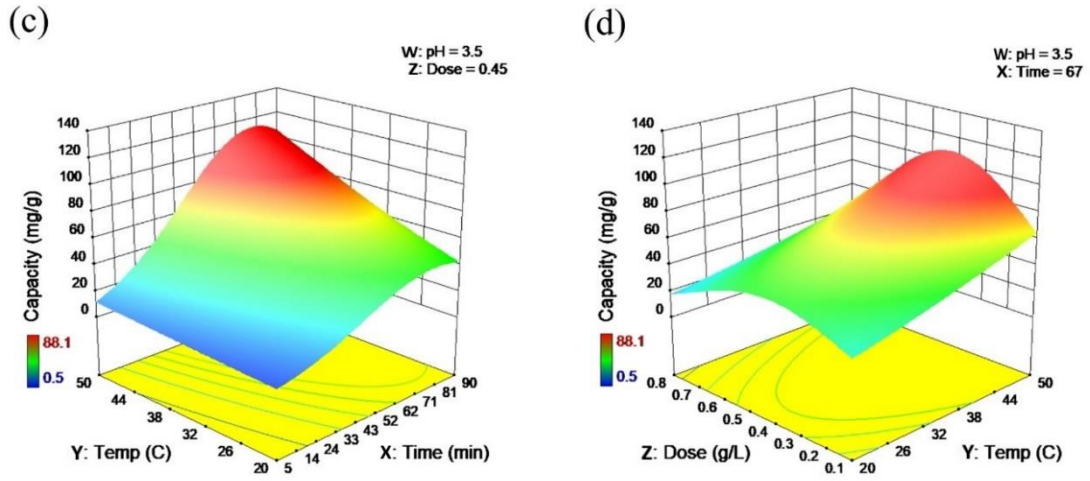


Figure 4. *Surface 3D Plot for adsorption parameters optimized using Response Surface Quadratic Model*

Optimization

Table 3 shows the optimum adsorption conditions determined using CCD-RSM. The model predicted the maximum adsorption capacity of 112 mg g^{-1} provided the process takes place for 64 min at pH 4.5 with an adsorbent dose of 0.4 g L^{-1} at 50 °C. Adsorption carried out at the optimized conditions yielded the adsorption capacity of 108 mg g^{-1} for Pb (II) ions. The observed adsorption capacity was 3.5% lower than the predicted value indicating a good fit for the model.

Table 3*. Optimized values of variables for the preparation of activation carbon from corn husk*

pH	Time (min)	Temp (°C)	Dose (g L^{-1})	Capacity (mg g^{-1})		% difference
				Predicted	Actual	
4.5	64	50	0.4	112	108	3.5

3.3. Adsorption Isotherms

Langmuir, Freundlich, and Temkin isotherm models evaluated the isotherm data using Equations (2), (3), and (4), respectively. The non-linear curve fitting method determined the model parameters

$$q_e = \left(\frac{K_L C_e}{1+K_L C_e}\right) q_m \tag{2}$$

$$q_e = K_f C_e^{1/n} \tag{3}$$

$$q_e = \frac{RT}{b_T} \ln(A_T C_e). \tag{4}$$

The plots of empirical isotherm data at selected temperatures along with the fitted curves are in Figure 5. It was evident from the plots that the Langmuir model did not fit the isotherm data. However, both Freundlich and Temkin models seem to work the data very well. Table 4 summarized the statistical parameters, including R^2, χ^2, and relative mean square deviation (RMSD). Langmuir's model had the least R^2 values and highest χ^2 and RSMD values suggesting that the model does not fit the experimental data. Freundlich model had the highest R^2 values and least χ^2 and RSMD values at all temperatures suggesting an excellent model for the isotherm data.

The Freundlich isotherm explains the adsorption process for heterogeneous surfaces. The term heterogeneous surface means that not all sites have the same affinity for the adsorbate [8]. The reactive sites with high bond energy occupy first, while as the process moves further, the bond energy of the active

sites decreases exponentially [9]. A plausible reason is the interaction of the already adsorbed particles with the incoming particles, making further adsorption difficult. The isotherm parameter, n, indicates the intensity of the adsorption process [10]. The 'n' values ranging from 1 to 10 indicate favorable conditions. The 'n' values in this study ranged from 5.655 to 8.006, suggesting that corn husk activated carbon is suitable for the adsorption of Pb(II) ions. However, an increase in 'n' value accompanies an increase in surface heterogeneity [11]. The 'n' values greater than five also concluded high surface heterogeneity. Furthermore, the temperature rise resulted in a decrease in the value of n, indicating a relative reduction in the heterogeneity of the surface.

Table 4. *Isotherm parameters for adsorption on corn husk sorbent*

Temperature (K)	298	303	308	313
	Langmuir			
qm (mg g^{-1})	180.23	197.05	224.26	251.67
K_L (L mg^{-1})	0.12214	0.12062	0.09961	0.08499
R_L	0.0604	0.0618	0.0731	0.0842
R^2	0.9968	0.9961	0.9972	0.9971
χ^2	40.32	50.69	43.02	54.67
RMSD	15.6	21.9	32.2	32.4
	Freundlich			
K_f (mg g^{-1})(L $mg^{-1})^{1/n}$	91.0113	93.4927	95.5385	98.6929
1/n	0.1249	0.1399	0.1601	0.1768
n	8.006	7.144	6.243	5.655
R^2	0.9998	0.9988	0.9991	0.9982
χ^2	1.30	12.34	10.44	15.80
RMSD	1.14	3.16	5.22	6.79
	Temkin			
At (L g^{-1})	51.275	26.288	10.131	5.477
b_T (kJ mol^{-1})	0.130	0.111	0.088	0.073
R^2	0.9996	0.9987	0.9988	0.9981
χ^2	3.21	13.38	14.19	28.11
RMSD	2.76	4.88	11.85	11.85

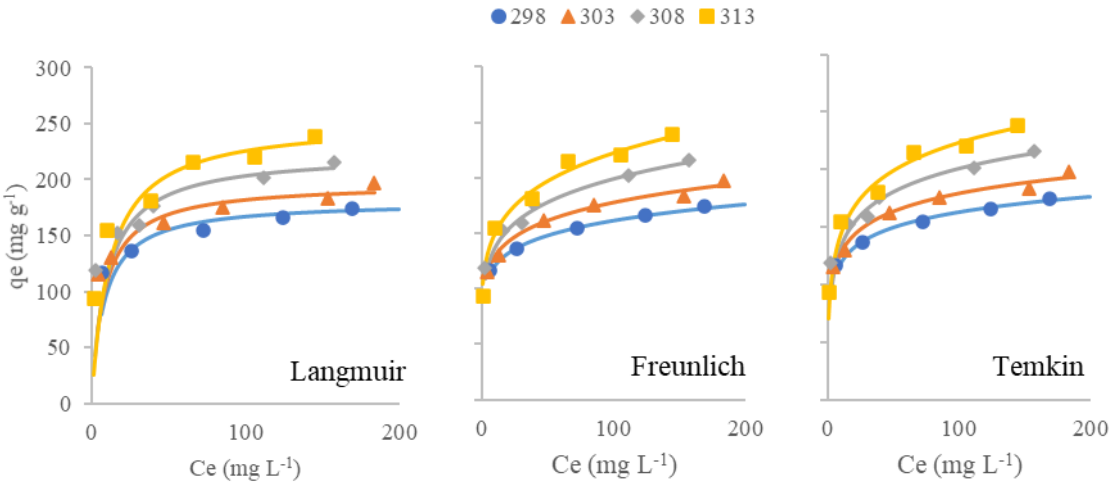


Figure 5. *Isotherm Plots of selected models for adsorption on corn husk sorbent*

3.4. Adsorption Kinetics

The kinetics models used to evaluate the kinetics data were pseudo-first-order, pseudo-second-order, and Weber and Morris intraparticle diffusion model. This study used non-linear curve fitting to determine the

kinetic parameters and the Levenberg Marquardt algorithm for the iterations. Figure 6 shows the plots of empirical data along with the fitted curves at the selected temperatures. The pseudo-second-order model fitted better than the pseudo-first-order model. The χ^2 for the pseudo-first-order model ranged from 30.06 to 34.86, whereas the range for the pseudo-second-order model was from 3.33 to 4.20. The values of statistical and kinetic parameters are tabulated in Table 5.

Pseudo-first-order: $q_t = q_e\left(1 - e^{-k_1 t}\right)$ (5)

Pseudo-second-order: $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$ (6)

Table 5*. Kinetics parameters for adsorption on corn husk sorbent*

Temperature (K)	298	303	308	313
Pseudo-first-order				
k_1 (min^{-1})	0.03223	0.03647	0.04205	0.05164
q_e (mg g^{-1})	151.5	148.6	146.5	140.2
χ^2	30.03	34.83	49.38	34.86
R^2	0.9788	0.9720	0.9536	0.9569
Pseudo-second-order				
k_2 (g mg^{-1} min^{-1})	1.98×10^{-4}	2.42×10^{-4}	3.02×10^{-4}	4.24×10^{-4}
q_e (mg g^{-1})	182.3	176.0	170.7	159.9
χ^2	3.33	2.23	4.00	4.20
R^2	0.9976	0.9982	0.9962	0.9948

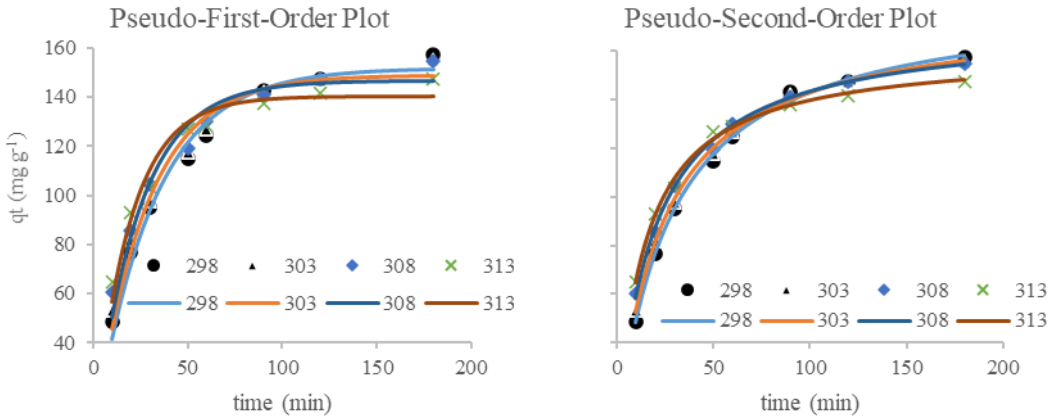


Figure 6*. Plots of Kinetics data fitted with selected kinetic models*

The Weber-Morris model predicts a linear qt versus $t^{0.5}$ plot if the adsorption mechanism is based solely on intraparticle diffusion. Figure 7 shows the Weber-Morris plot for the adsorption of Pb(II) ions on corn husk activated carbon. It showed multilinearity which indicated the presence of different types of intraparticle diffusions. The parameters for the model and their values are in Table 6. Pb(II) adsorption on adsorbent started fast with higher values of a diffusion-constant k_{id} followed by a slower process with a lower rate constant. A possible explanation of the quick start is the external mass transfer, which is a faster diffusion of adsorbate to the surface of the adsorbent. The subsequent slow process can be the inner diffusion of adsorbate into macro, meso, and micropores. The diffusion rate constants were temperature-dependent and

decreased with an increase in temperature. It might be because an increase in temperature increases the kinetic energy of particles, which ultimately favors the chaos in the system and disturbs the diffusion of adsorbate into the adsorbent.

Table 6*. Parameters for Weber-Morris intraparticle diffusion model*

Temperature (K)	298	303	308	313
Adsorption process 01				
k_{id} (mg g^{-1} $min^{-0.5}$)	16.112	15.559	14.629	13.928
C (mg g^{-1})	1.8688	8.5988	18.24	25.592
Adsorption process 02				
k_{id} (mg g^{-1} $min^{-0.5}$)	3.6964	3.322	3.4257	2.4596
C (mg g^{-1})	107.46	110.62	109.14	114.47

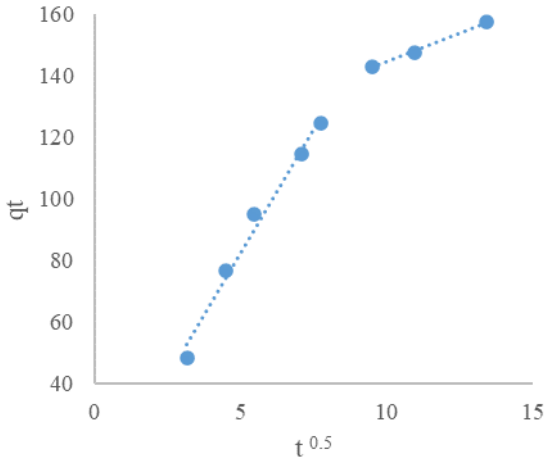


Figure 7*. A plot of Weber-Morris intraparticle diffusion model*

3.5. Adsorption Thermodynamics

Isotherm and kinetics data obtained at different temperatures yielded essential thermodynamic parameters. The negative ΔG values, calculated using Equation (7), proved the spontaneous nature of adsorption. An increase in temperature made the values more negative, indicating that heating the system favored the adsorption process. Table 7 summarized the isotherm data and the ΔG values obtained from the $\ln K_c$ versus 1/T plot. The ΔH value for the Pb(II) adsorption on corn husk activated carbon was 43.78 kJ mol^{-1}. The positive value concluded that the adsorption was endothermic. The adsorption was physisorption as the ΔH value was less than 80 kJ mol^{-1} – the minimum enthalpy change for chemisorption [12]. The ΔS was 154.2 J $mol\ K^{-1}$, a positive value that indicated an increase in disorder due to adsorption. The kinetics data also yielded the activation energy (E_a) when processed using the Arrhenius relation, shown as Equation (8). The slope of $\ln k_2$ against 1/T gave a value of 30.17 kJ mol^{-1} for the activation energy of the adsorption process.

$$\Delta G^{\circ} = -RT\ln K_c \tag{7}$$

$$\ln k_2 = \ln k_o - \frac{E_a}{R}\frac{1}{T} \tag{8}$$

Table 7*. Thermodynamic parameters obtained using lnKc and 1/T at selected temperatures*

1/T	lnK_c	ΔG (kJ mol^{-1})
0.003356	0.76000	-1.88
0.003300	1.23735	-3.11
0.003247	1.64428	-4.21
0.003195	1.55947	-4.05

4. CONCLUSION

This study comprised the optimization of Pb(II) adsorption onto the corn husk sorbent using the central composited design for the response surface method. The selected statistical method was found excellent for the optimization of the adsorption processes. The study concluded that the Response Surface Method significantly reduces the number of trials required for optimization, which ultimately reduced the use of chemicals and time. The prepared activated carbon possessed tremendous potential for the removal of Pb(II) ions. Moreover, the optimization of the adsorption process with the least quantity of reagents would result in an environmentally friendly optimization method.

ACKNOWLEDGMENT

The authors acknowledge the Dean Faculty of Science, University of Karachi, for providing the research grant.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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