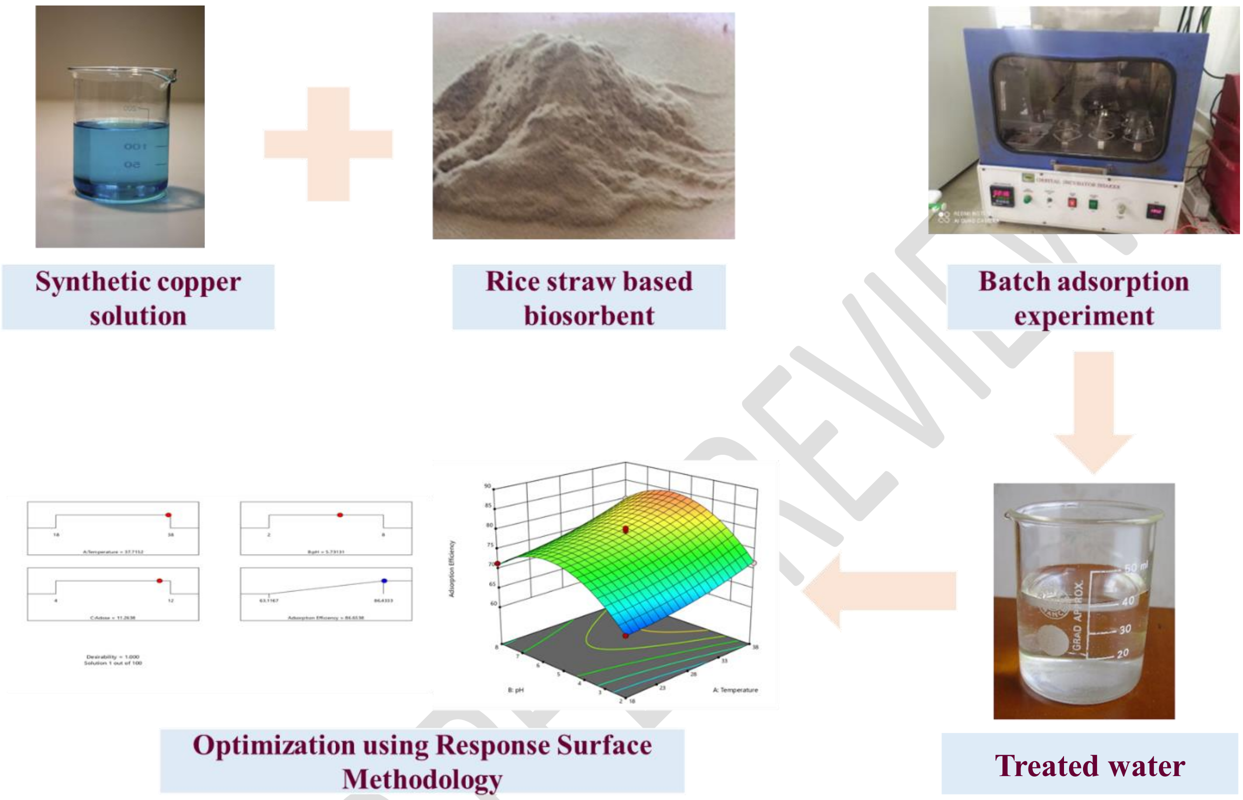
Optimizing Copper Adsorption from Aqueous Solutions with Modified Rice Straw Using Response Surface Methodology.

Abstract

Heavy metal contamination poses an impulsive threat to human and aquatic life and ecosystem health. To ensure safe and sustainable water accessibility, biosorption with low-cost adsorbents is acknowledged as a promising approach for the remediation of noxious pollutants. The current study was oriented to appraise the performance of modified rice straw for copper adsorption in hand with the optimization of its operational parameters. RSM-based Box-Behnken design was employed to optimize the operational variables encircling temperature, pH, and adsorbent dose. The results elucidated that the generated model exhibited an R-squared of 0.98, reflecting its validity in describing the experimental data well. The optimized conditions for attaining maximum copper adsorption were marked to be a temperature of 37.71, a solution pH of 5.7, and an adsorbent dose of 11.26. Under these optimized conditions, the adsorption efficiency was marked to be 86.65 %. The experimental adsorption efficiency under these conditions was noted to be approximately 86.43 %, reflecting the suitability of the RSM-based Box-Behnken design. Conclusively, it can be inferred that acid modified rice straw offers a promising low cost adsorbent for remediation of heavy metals in accordance with the principles of green chemistry.

Key Words: Copper, Adsorption, Rice straw, Optimization, RSM

Graphical Abstract



Introduction

Water constitutes a prime resource for the existence of life on earth and access to fresh water is terrible for humans as well as the ecosystem. Water comprises the core of sustainable development and is instrumental for socio-economic development, food and energy production, sound ecosystems and for human existence *per se* (Connor, 2015). In addition, water represents the core of climate change adaptation, illustrating a key bond amid society and the environment. Nevertheless, the water quality has deteriorated in response to population expansion, rapid industrialization, urban sprawl, and ruthless exploitation of natural resource base in recent decades (Carolin *et al*., 2017). Heavy metals constitute a predominant element of water pollution on account of being toxic and non-biodegradable (Briffa *et al*., 2020).

Among these toxic heavy metals, copper (II) finds its place despite being an instrumental element in the human body and various biological processes of animals. Excessive consumption of copper at elevated concentrations is marked to induce toxicological concerns, encapsulating cramps, convulsions, vomiting, and even death (Fu and Wang, 2011). The contamination triggered by copper ions might result in keratinization, and tingling sensations, and has been acknowledged for mutagenic and carcinogenic properties (Dias *et al*., 2007). Consequently, it is imperative to remediate the toxic metal ions from wastewater before discharge to avoid additional detrimental consequences. Conventional methods like electrocoagulation, membrane filtration, ion exchange, chemical precipitation, etc. have been cast-off for heavy metal remediation from wastewater. However, these techniques exhibit certain disadvantages such as high energy requirements, high cost, low efficiency, and precipitation of toxic substances (Hussain *et al*., 2021). Given this, the employment of economically effective and eco-friendly interventions is imperative to remediate the heavy metals from wastewater.

Adsorption stands out as one of the most promising approaches on account of its simplicity, remarkable efficiency in removing pollutants across a broad pH spectrum, and economic feasibility. The engagement of biomass-based low-cost adsorbents adds to its application for being readily accessible, inexpensive, and environmentally friendly. The exploitation of plant-based adsorbents owes their remediation potential to the prevalence of different functional groups encompassing cellulose, hemicelluloses, lignin, pectin, and other extracts that effectively adsorb metal ions (Raji *et al*., 2023). The acid treatment of these low-cost adsorbents induces a positive charge on the biosorbent surface, which eventually amplifies the adsorption of positively charged metal ions (Abegunde *et al*., 2020). However, the process of adsorption is governed by various operational parameters that need to be optimized to reduce the required experiment number and reduce process inconsistency with an overall reduction in the cost of wastewater treatment (Chattoraj *et al*., 2016). Response surface methodology (RSM)- a statistical approach intends to design experiments, develop empirical models, and optimize its operating conditions to attain a desirable solution (Lamidi *et al*., 2022). RSM reduces the requisite number of experiments apart from appraising the interactive effects of operational variables, thereby possessing an edge over conventional approaches (Aydar, 2018). Against this backdrop, the current study intends to devise experiments and evaluate the adsorption of copper ions using modified rice straw.

Materials and Methods

Biosorbent Preparation

Rice straw as a waste by-product was procured from a local agricultural field at the Faculty of Agriculture, SKUAST-Kashmir, Wadoora, Sopore. The acquired adsorbent was cleansed with tap water, followed by several washings with deionized water. Following this, the adsorbent was oven-dried at 80^{o}C until constant weight and ground into small particle sizes using a grinding mill. The pulverized adsorbent was sieved through 35 mesh sieve and kept in air-tight polyethylene bags for further laboratory analysis.

Modification of Biosorbent

20 grams of processed rice straw was treated with 400 ml of 0.1N HNO_3. After a brief soaking period, the mixture was agitated at 50^{o}C in a thermostatic shaker at 200 rpm for 4 hours. Ensuing this, the treated adsorbent was subject to several washings with deionized water followed by its oven drying at 100^{o}C for 2 hours. The dried samples were stored for further laboratory analysis.

Adsorption of copper ions

Copper adsorption was evaluated using batch adsorption technique as described by Loebenstein (1962). In this technique a known adsorbent amount was agitated with 50 ml Cu (II) solution possessing an invariable concentration of 60 mg L^{-1}. and desired pH. The imprints of operational parameters encasing temperature, pH, and adsorbent dose were evaluated. The adsorption efficiency of copper ions was determined using the following equations

$$AE = (C_i - C_e)/C_i \times 100 \ldots\ldots\ldots\ldots (1)$$

Where,

AE = adsorption efficiency (%) C_i, and C_e = initial and equilibrium metal ion concentration (mg L^{-1}), respectively. V = volume of Cu (II) solution (L) and m = mass of adsorbent in grams.

Experimental Design

To explore and optimize the effect of operational variables, response surface methodology was employed. The execution was done following the experiments designed by RSM-based Box-Behnken design comprising five replications at central points and 17 runs in total using Design Expert software version 13.0.15.

The response (copper adsorption) was expressed as a function of operating variables using the second-order polynomial model:

$$Y = \beta_o + \sum_{i=0}^{k} \beta_i X_i \sum_{i=0}^{k} \beta_{ii} X_i^{\,2} + \sum_{1\le i\le j}^{k} \beta_{ij} X_i Y_j + \varepsilon \ldots\ldots.(2)$$

Where Y is the predicted response (Adsorption efficiency), X_i is the operating variable, β_o is the constant coefficient, β_i, and β_{ii} are the linear and quadratic coefficients of input variables, β_{ij} is the interaction coefficient of X_i and X_j input variables and ε is the random error.

Kinetic Study

The kinetic behaviour of adsorbates on adsorbents was appraised using the reaction models such as Lagergren's Pseudo-first-order model, Pseudo-second-order kinetics, and Elovich model, and the adsorption diffusion models encircling the Intraparticle diffusion model and Boyd model.

Model	Equation
Pseudo-first-order model	$\ln (Q_e - Q_t) = \ln Q_e - Kt$

Pseudo-second-order model	$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t$
Elovich model	$Qt = \beta \ln(\alpha\beta) - \ln(t)$
Intraparticle diffusion model	$Qt = K_{ID}\sqrt{t} + I$
Boyd model	Bt= -0.4978 - ln (1-Qt/Qe)

Isotherm Study

An adsorption isotherm study was performed at a temperature of 38 ^{o}C for each metal ion solution. An adsorbent dose of 8 g L^{-1} was agitated with a 50 ml metal ion solution in a thermostatic shaker at a pH of 4 for 180 min. The acquired observations were analyzed using Langmuir, Freundlich, and Temkin isotherm models.

Isotherm	Equation
Langmuir Isotherm	$\frac{C_e}{q_e} = \frac{1}{b_o q_m} + \frac{1}{q_m} C_e$
Freundlich Isotherm	$ln q_e = ln K_F + \frac{1}{n} ln C_e$
Temkin Isotherm	$q_e = \frac{RT}{b} ln\ K_T + \frac{RT}{b} ln\ C_e$

Thermodynamic Study

The acquired experimental data from the adsorption study was employed to determine the thermodynamic parameters encircling Gibbs free energy change (ΔG), change in enthalpy (ΔH), change in entropy (ΔS), Isosteric heat of adsorption (ΔH_X), sticking probability (S*) and activation energy (E_a).

Gibbs Free Energy	ΔG^o= -RT. ln K	ΔH and ΔS were calculatedfrom the slope and intercept of the plots of ln K versus 1/T.
Isosteric Heat of Adsorption (ΔH_X)	Clausius Claperyron Equation: $\frac{d\ (\ln Ce)}{dT} = \frac{\Delta Hx}{RT^2}$	A plot of ln C_e vs 1/T

Sticking Probability (S*)	$n\ (1-\theta) = \ln S^* \frac{Ea}{RT}$	Slope and intercept of ln (1- θ) vs1/T give Sticking probability and Activation energy, respectively.

Results and discussion

Optimization of copper adsorption

The experiments designed by RSM-based Box-Behnken design are portrayed in Table 1. The influence of operational variables encircling temperature (18-38^{o}C), pH (2-8), and adsorbent dose (4-12 g L^{-1}). The model generated for copper adsorption, illustrating the relationship between predicted response and operational variables is:

Adsorption Efficiency = +39.81162- 0.217136 Temperature+10.27065 pH+1.19552 Adose +0.016806 Temperature * pH - 0.020000 Temperature*Adose - 0.057292 pH * Adose+ 0.012358 Temperature^2 - 0.910370 pH^2 + 0.028281 Adose^2

Table 1: RSM-based Box-Behnken experiment for copper adsorption

*AMRS-Acid-Modified Rice Straw

Analysis of Variance

ANOVA results for copper adsorption in Table 2 show the model significance with an F-value of 42.77 and p-value < 0.05. Modified rice straw adsorption had significant terms A, B, C, A^2, and B^2. Lack-of-Fit F-value was 1.77, and the p-value was 0.29, indicating the model fit well (Marrane *et al*., 2022). Key factors are temperature, pH, and adsorbent dose affecting copper removal efficiency. Model fit assessed by R-squared value. ANOVA results showed R^2 = 0.98, indicating strong agreement between observed and predicted values. Figure 1 illustrates the comparison plot of experimental and model values, showing close alignment and validating the RSM-based Box Behnken model's accuracy.

		Factor 1	Factor 2	Factor 3	Response 1	Response 1
Std.	Run	A:Temperature	B: pH	C:Adose	Actual Response AE-AMRS %	Predicted Response AE-AMRS %
1	1	18	2	8	65.05	64.99
14	2	28	5	8	79.80	78.97
4	3	38	8	8	79.98	80.04
10	4	28	8	4	71.25	72.25
15	5	28	5	8	78.45	78.97
6	6	38	5	4	83.30	82.24
5	7	18	5	4	73.28	72.66
8	8	38	5	12	86.43	87.05
16	9	28	5	8	80.43	78.97
11	10	28	2	12	72.58	71.59
3	11	18	8	8	71.43	71.06
13	12	28	5	8	78.23	78.97
12	13	28	8	12	77.97	77.29
7	14	18	5	12	79.62	80.68
17	15	28	5	8	77.94	78.97
9	16	28	2	4	63.12	63.80
2	17	38	2	8	71.58	71.96

Table 2: Analysis of variance for RSM-based quadratic models for cadmium adsorption

Source	Sum of Squares	Df	Mean Square	F-value	p-value

Model	600.56	9	66.73	42.77	< 0.0001	significant
A-Temperature	127.33	1	127.33	81.61	< 0.0001	
B-pH	100.11	1	100.11	64.16	< 0.0001	
C-Adose	82.24	1	82.24	52.71	0.0002	
AB	1.02	1	1.02	0.6516	0.4461	
AC	2.56	1	2.56	1.64	0.2410	
BC	1.89	1	1.89	1.21	0.3074	
A^2	6.43	1	6.43	4.12	0.0819	
B^2	282.66	1	282.66	181.16	< 0.0001	
C^2	0.8621	1	0.8621	0.5525	0.4815	
Residual	10.92	7	1.56			
Lack of Fit	6.22	3	2.07	1.77	0.2924	not significant
Pure Error	4.70	4	1.17			
Cor Total	611.48	16				

R^2-0.98 Adjusted R^2-0.95 Predicted R^2-0.82 Adeq precision-24.27

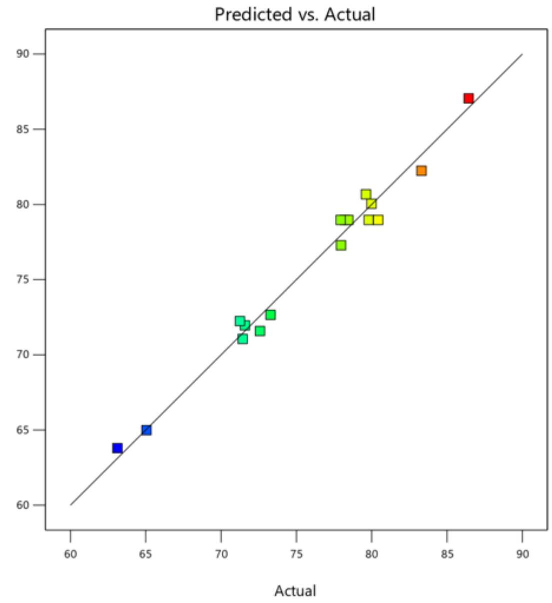
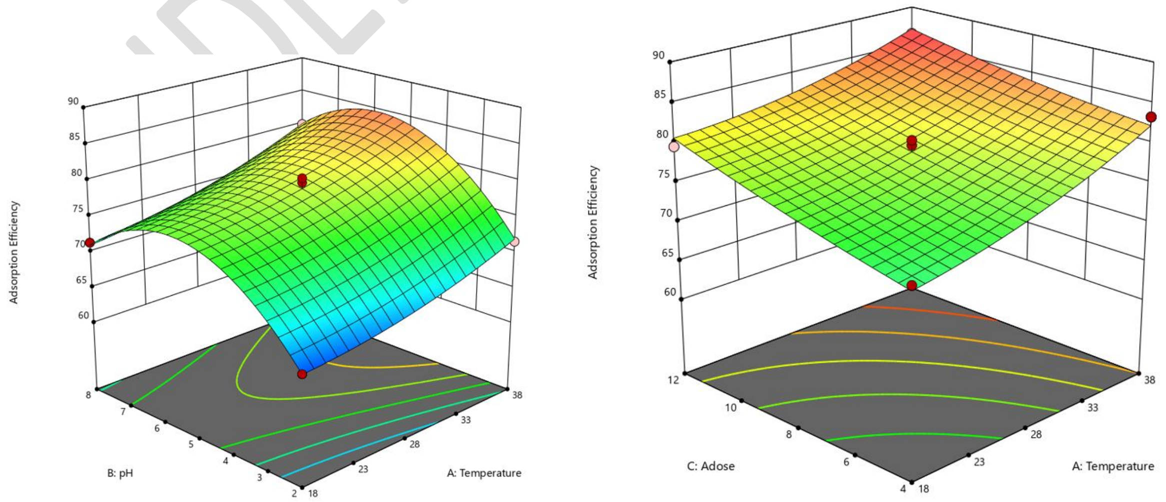


Figure 1: Comparison plot between actual observations and model values

Effect of Operational Variables

Figure 2 (a, b) represents the effect of temperature on copper adsorption efficiency. The inferences elucidated that with an increase in temperature from 18 to 38 ^{o}C, the removal efficiency of copper increased. The increased removal efficiency at elevated temperatures might be accounted to the higher kinetic energy and enhanced diffusion of metal ions across boundary layers as well as adsorbent surface (Pan *et al*., 2022). Furthermore, the adsorption efficiency exhibited a decline with an increase in solution pH. Comparable findings have been put forward by Elkhaleefa *et al*. (2021) and Cruz-Lopes *et al*. (2021). The maximum copper removal was marked at a pH range of 4-6. Solution pH directly associates with the preponderance of H^+ ions, which compete with the metal ions for adsorption (Lecca-Caballero *et al*., 2023). The copper adsorption was marked to increase with an increase in adsorbent dose from 4 to 12 g L^{-1}. The increased adsorption efficiency might be accredited to the prevalence of more binding sites for metal adsorption at higher adsorbent doses. Comparable dependence has been put forward by Al-Qahtani (2016) and Al-Senani and Al-Fawzan (2018).



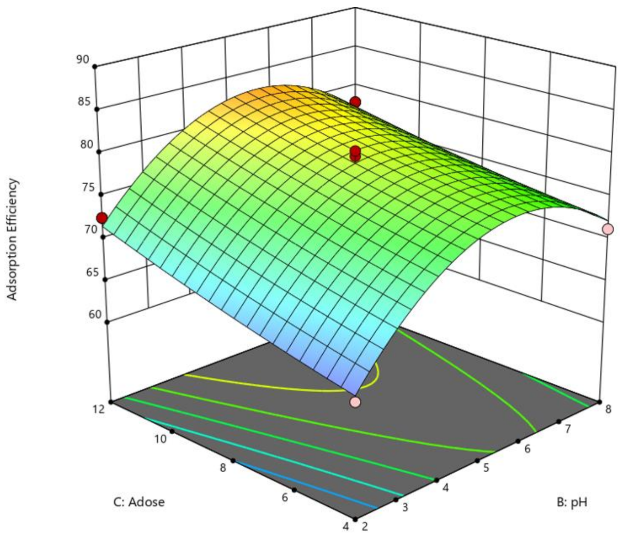


Figure 2: 3d response surface plots for copper adsorption, illustrating the effect of temperature (a, b), pH (a, c), and adsorbent dose (b, c).

Optimization using the desirability function

Numerical optimization of response surface methodology was employed to achieve a desirable solution for copper adsorption at different combinations of operational variables. Out of 100 solutions, a solution possessing high desirability was chosen. A number of solutions with high desirability obtained for copper adsorption under varying operational parameters validate the applicability of respective adsorbent (Fertu *et al*., 2022). From Figure 3, it can be inferred that to attain maximum copper removal efficiency (desirability=1.00), the operational variables need to be tuned at a temperature of 37.71, a solution pH of 5.7, and an adsorbent dose of 11.26. Under these optimized conditions, the adsorption efficiency was marked to be 86.65 %. The experimental adsorption efficiency under these conditions was noted to be approximately 86.43 %, reflecting the suitability of the RSM-based Box-Behnken design.

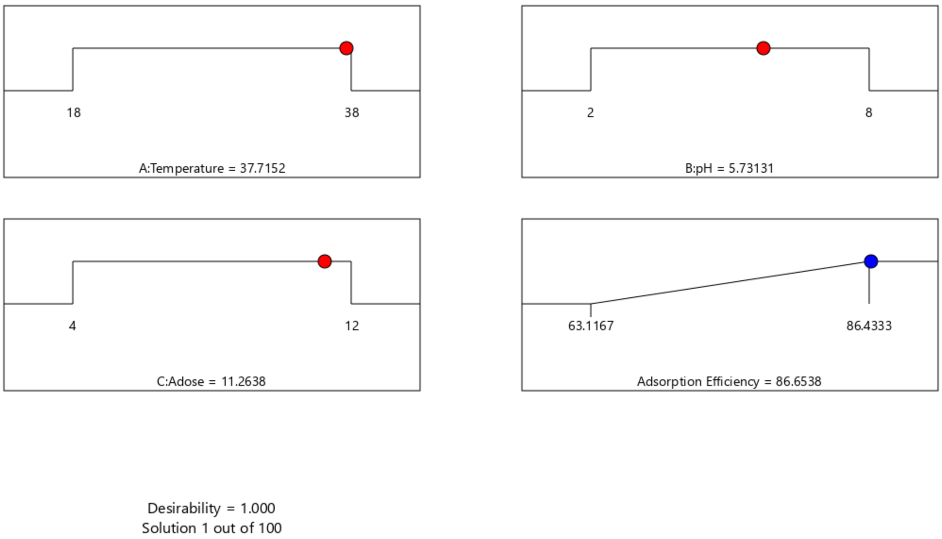


Figure 3: Optimization of copper adsorption using acid-modified rice straw

Kinetic Study

Kinetic models describe the mechanism of sorption and the rate-limiting steps entailed in the adsorption process (Ebelegi *et al*., 2020). The inferences presented in Table 3 elucidated that pseudo-first-order and pseudo-second-order models possessed high R-squared values (0.99) compared to other kinetic models. The q_e values predicted by pseudo-first order and pseudo-second order were closely approximated to the experimental values, suggesting that the model described the experimental data well (Bullen *et al*., 2021). The alignment of experimental data with the pseudo-second-order kinetic model signifies that the adsorption of the copper ions onto the modified rice straw is governed by chemisorption with no involvement of mass transfer in solution (Arshadi *et al*., 2014). The adsorption of metal ions possessed an initial adsorption rate of mg/(g min) for over acid-modified rice straw.

Table 3: Kinetic models for the adsorption of Cu (II) on acid-modified rice straw

Operational conditions: pH-4; Temperature-38^{o}C; Adsorbent dose-12 g L^{-1}

Model	Model Parameters	Cu (II)

	q_{exp}	**4.32**
Pseudo-first order kinetics	q_e	4.19
	k_1	0.052
	R^2	0.99
Pseudo-second order kinetics	q_e	4.55
	k_2	0.020
	R^2	0.99
Elovich model	α	1.17
	β	1.02
	R^2	0.98
Intraparticle diffusion	k_p	0.307
	R^2	0.83
Boyd model	R^2	0.81

Adsorption Isotherms

Adsorption isotherms reflect the amount of adsorbate retained by the adsorbent to the concentration in solution at equilibrium (Raji *et al*., 2023). The inferences of employed adsorption isotherms encircling Langmuir, Freundlich, and Temkin isotherms for copper adsorption are portrayed in Table 4**.** The correlation coefficients varied from 0.96-0.99 for copper adsorption using acid-modified rice straw. The R-squared values (goodness of fit criteria) for evaluated isotherms revealed that Langmuir isotherm best reproduced the experimental data for copper adsorption, illustrating a monolayer coverage of metal ions onto the adsorbent surface. The q_m (mg/g) and *b* (L/mg) of the model represent the maximum monolayer adsorption capacity and adsorption energy, respectively. The 1/n values for the copper adsorption are all less than 2, illustrating that they are easily absorbed by the acid-modified rice straw (Wang *et al*., 2020). Unlike the Langmuir and Freundlich isotherm, Temkin isotherm model entails the interactions between adsorbent and the metal ions to be adsorbed where model undertakes the free energy of sorption as a function of the surface coverage. In this model b is a constant affiliated with the heat of adsorption, while K_T is a Temkin binding constant (Khamwichit *et al*., 2022).

Table 4: Adsorption Isotherms for the adsorption of Cu (II) on acid-modified rice straw

Model	Model Parameters	Cu (II)
Langmuir	q_m	1.142
	b_o	0.023
	R^2	0.99
Freundlich	**1/n**	0.952
	k_f	1.242
	R^2	0.98
Temkin	k_T	0.472
	B	6.971
	R^2	0.96

Thermodynamic Study

The negative values of ΔG reflected that the adsorption process of Cu (II) onto acid-modified rice straw is thermodynamically favorable and spontaneous. The positive values of ΔH suggested that the adsorption process is endothermic in nature. Furthermore, the negative values of ΔS indicated an increase in the randomness and disorder at the surface of the adsorbent. Similar dependence has been put forward by Manirethan *et al*. (2018) and Tighadouini *et al*. (2022).

Table 5: Thermodynamic parameters for adsorption of Cu (II) on acid-modified rice straw

Operational conditions: pH-4 Adsorbent dose-12 g L^{-1}

Metal Ion	Temperature (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)	ΔH_X (J/mol)	S^*	E_a (KJ/mol)
Cu (II)	291	-15.6190	14.28036	53.72257	1839.1	0.000371	15.29028
	301	-16.1562					
	311	-16.6934					

Major Constraints and Future Directions

Response Surface Methodology provides valuable insights into the metal adsorption using biomass based adsorbents, however, there are certain limitations that need to addressed. The primary constraint is the narrow experimental range of RSM technique. Another constraint of using response surface methodology is its dependency on the second-order polynomial for modeling, which is inadequate to represent all curvatures in the operating system. To circumvent these constraints, RSM needs to be integrated with other optimization techniques and machine learning approaches to improve the robustness of optimization process. In addition, there is a call for inclusion of cost analysis while optimizing a particular system/process. The regeneration of adsorbents in a fixed bed column can be also appraised studied to alleviate the problem of adsorbent disposal after use.

Conclusion

The performance of acid-modified rice straw was appraised using batch adsorption technique. The acid modified rice straw was gauged for optimization of copper adsorption using RSM based Box-Behnken design. The developed polynomial quadratic models illustrated a healthy confirmation with the experimental data at 95% significance level. This was backed by attaining a high R-squared value ($R^2 = 0.98$), while further validation was established through analysis of variance (ANOVA), up-holding the cogency of the employed model. The optimal conditions for achieving a solution with high desirability (1.00) were marked to be a temperature of 37.71, a solution pH of 5.7, and an adsorbent dose of 11.26, marking 86.65 % of copper removal. The experimental adsorption efficiency under these conditions was noted to be approximately 86.43 %, reflecting that the aptness of the RSM-based Box-Behnken design.

Conclusively, it can be inferred that acid modified rice straw offers a promising low cost adsorbent for remediation of heavy metals in accordance with the principles of green chemistry.

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