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Optimization of Hexavalent Chromium Removal from Aqueous Solution by Ascorbic Acid Treated Sugarcane Bagasse

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The study focuses on developing an effective adsorbent for the removal of Hexavalent chromium from aqueous solutions. It utilizes chemically modified sugarcane bagasse cellulose, enhanced with ascorbic acid, as the adsorbent material. A comprehensive model was established to examine both the individual and combined effects of different variables on the adsorption process, employing a central composite rotatable experimental design rooted in response surface methodology (RSM). The model underwent experimental verification and statistical validation through analysis of variance (ANOVA) before determining the optimal conditions for Hexavalent chromium removal. The optimal parameters identified were an initial Hexavalent chromium concentration of 100 ppm, a pH of 2, and a modified sugarcane bagasse dosage of 0.5 g/L. Under these conditions, an impressive removal rate of 162 mg/g of Hexavalent chromium was achieved. The findings were consistent with the optimization study, and the adsorption process was well described by the Langmuir model. This research highlights the potential of utilizing agricultural waste, modified in a straightforward manner, to create a cost-effective adsorbent for heavy metal removal from water. Nevertheless, some limitations were observed regarding the material's reuse potential and its adsorption capacity in complex wastewater conditions.

Keywords: sugarcane bagasse, hexavalent chromium, ascorbic acid, removal, response surface methodology (RSM).

Introduction

Chromium compounds are frequently detected as toxicants in aquatic environments. The extensive use of chromium in various industries inevitably releases substantial amounts of Hexavalent chromium into the environment (Al-Sulaimani and Priy, 2017; Bandara et al., 2020). According to the International Development Association, over 95% of chromium is consumed by the metallurgical industry, approximately 3% by the refractory and foundry industries, and about 2% by chemical manufacturers. Chromium is primarily used in producing stainless steel, alloy steel, and non-ferrous alloys. Additionally, chromium compounds are widely applied in fields such as textile dyeing, paint production, and wood preservation.

The biotoxicity and diffusion rate of chromium in water and soil are largely determined by its valence state. The major and most stable forms in water/wastewater are trivalent chromium (Cr(III)) and hexavalent chromium (Hexavalent chromium). However, Hexavalent chromium is the primary contributor to chromium contamination in the environment (Bandara et al., 2020; Bhaumik et al., 2013; Cimino et al., 2000). Hexavalent chromium is significantly more toxic and persistent than Cr(III). Furthermore, Hexavalent chromium oxidizes readily in acidic conditions, making it easier to reduce to Cr(III). In contrast, Cr(III) is generally non-toxic and plays an essential role in animal and human metabolism. On the other hand, Hexavalent chromium is highly hazardous due to its mutagenic and carcinogenic properties, posing a severe risk to living organisms (Demiral et al., 2008; Ezeonuegbu et al., 2021; Fan et al., 2017)

Numerous disastrous Hexavalent chromium exposures have been documented worldwide. For instance, the US EPA has identified Hexavalent chromium as one of 129 critical contaminants (Garg et al., 2007; Hamadi et al., 2001; Haque et al., 2022). Hexavalent chromium exposure has been linked to damage in several organs, including the lungs, kidneys, and liver, as well as to a weakened immune system (Haroon et al., 2017). The permissible levels of hexavalent chromium have been set by the US EPA and WHO at 0.1 mg/L and 0.05 mg/L, respectively (Huong and Trang, 2023; Jeřábková et al., 2018; Labied et al., 2018).

Various treatment techniques can be employed to control Hexavalent chromium levels in water. Among these, adsorption is particularly popular due to its effectiveness, practicality, minimal environmental impact, and ease of use. However, the high costs associated with the repeated replacement of adsorbent materials limit its commercial viability (Majeed et al., 2014; Moughaoui et al., 2017; University of Massachusetts Lowell). To enhance the economic feasibility of adsorption, low-cost materials, such as agricultural waste, can be utilized as adsorbents. Agricultural wastes including rice husk (Haroon et al., 2017), wheat-rice bran (Bandara et al., 2020), sawdust (Garg et al., 2007; Jeřábková et al., 2018), and tree bark (Narendra and Sreedevi, 2021) have been investigated for their potential in Hexavalent chromium adsorption. Modified materials, such as rice husk treated with sorbic acid for Hexavalent chromium adsorption (Huong and Trang, 2023) and maize cobs for removing zinc (II) and Hexavalent chromium from wastewater (Kulmedov and Mohammed, 2023), have also shown promising results. Moreover, advanced composites like Cu/Ni bimetallic nanoparticles embedded in sugarcane pulp biochar have demonstrated efficacy in dye removal (Mengqi et al., 2023).

Among these materials, sugarcane bagasse has shown a high potential for removing Hexavalent chromium from aqueous solutions. Sugarcane (Saccharum officinarum), a widely cultivated tropical crop, which is a major raw material for the global sugar industry, with its cultivation concentrated in both developed and developing countries (Demiral et al., 2008; Fan et al., 2017; Hamadi et al., 2001). Sugarcane bagasse contains approximately 42% cellulose, 25% hemicellulose, and 20% lignin. According to the Organization for Economic Co-operation and Development (OECD) report for 2022, developed countries produced 85 million tonnes (Mt) of sugarcane, while developing countries produced 1688 Mt (Labied et al., 2018; Oldfield et al., 2016; Phaenark et al., 2023). Sugarcane production is expected to increase in the coming years, leading to more available waste materials.

Bagasse, a major agricultural byproduct, is widely used for various purposes, including as raw material for paper production, fuel, and biodegradable packaging (Phaenark et al., 2023; Srivastava et al., 2007; Yang et al., 2013). Its potential as a heavy metal adsorbent has been demonstrated in numerous studies. For instance, Ezeonuegbu et al. reported that sugarcane bagasse adsorbed 89.31% of Pb(II) and 96.33% of Ni(II) under optimal conditions (Ezeonuegbu et al., 2021). Additionally, studies by Yang and Yogeshwaran and Priya highlighted impressive removal efficiencies, with bagasse adsorbing 95.6% of Hexavalent chromium, 87.2% of Pb(II), and 83.3% of Zn(II), respectively (Srivastava and Priya, 2007; Yang et al., 2013).

Several factors influence the adsorption process, including pH, initial Hexavalent chromium concentration, and adsorbent dosage. The response surface methodology (RSM) with a central composite rotatable design (CCRD) was used to simulate and optimize Hexavalent chromium removal under varying conditions (Yogeshwaran and Priya, 2021; Martino et al., 2015; Mourabet et al., 2017; Korbahti and Rauf, 2008).

This study presents compelling evidence on how various factors affect the adsorption process, aiming to establish the optimal parameters for effectively removing hexavalent chromium (Hexavalent chromium). Sugarcane bagasse (SB) underwent chemical modification with ascorbic acid to produce treated sugarcane bagasse (T-SB), enhancing its adsorption capabilities. By evaluating four critical factors pH, contact time, adsorbent dosage, and the initial concentration of the adsorbate we can significantly maximize Hexavalent chromium adsorption efficiency.

To substantiate our findings, we analyzed the modified material using advanced techniques like Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX). These methods provide a thorough understanding of the Hexavalent chromium removal mechanism. Additionally, we conducted isotherm and kinetic studies to gauge T-SB's adsorption capacity in aqueous solutions. We believe that this research will pave the way for developing innovative and durable solutions to effectively eliminate hexavalent chromium from wastewater, addressing a critical environmental issue.

Methods

Materials

Potassium dichromate ($K_2Cr_2O_7$) derives from the Xilong branch, in China. Ascorbic acid ($C_6H_8O_6$ purity 99.7%) was purchased from Arshine Group C., Ltd. Sodium hydroxide (NaOH) and hydrochloric acid (HCl 37%) were bought from Weifang Js Trading Co., Ltd. Kanto Chemical Co., Inc in Japan is the supplier for 1,5-diphenyl carbohydrazide (DCP). Sulfuric acid was provided by Hawkins, Inc. Acetone ($C_3H_6O_3$) was purchased from Hai Ha Chemical company.

Equipment

UV-vis spectrophotometer model DR2800 for checking hexavalent chromium in the residual solution. FTIR 4700/JASCO were used to explore the characteristic pattern of absorption bands clearly indicates a change in the material's composition or the presence of contamination. TESCAN VEGA Compact Scanning Electron Microscopy – SEM machine shows the morphological material under high magnification. SHIMAZU EDX-LE PLUS machine used to determine the content of elements in materials. Besides, our research used some basic machine such as: magnetic stirrers, oven, pH meter, blender, etc.

Preperation treated sugarcane bagasses

Firstly, sugarcane bagasse was collected from a local market in Hanoi, Vietnam. To remove contaminants and pigments, the material was thoroughly washed multiple times with hot water until the rinse water ran clear, as residual color could affect the experimental results. The sugarcane bagasse was then dried at 70°C for several days to ensure complete removal of moisture.

For chemical treatment, the pretreated material was soaked and stirred in a 1M ascorbic acid solution for 24 hours. It was subsequently rinsed with distilled water until the pH reached neutral. The treated adsorbent was dried again at 70°C until all moisture was removed, and this drying step was repeated a few times to ensure consistency.

To achieve the desired particle size for the final adsorbent (0.5 mm), the sugarcane bagasse was milled and sieved. The finished adsorbent was stored in a plastic bag for later use (*Material treatment processing – supplementary data*).

Characterization of sugarcane bagasse and treated sugarcane bagasse with ascorbic acid

Using JSM-6500 (JEOL, Japan), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) were implemented to analyze the morphological structure and elemental makeup of the adsorbents. FTIR (Nicolet iS5, ThermoFisher Scientific, US) was performed to analyze the functional groups present in the investigated samples.

Experimental design and model development

The study employed a central composite rotatable design (CCRD) based on response surface methodology (RSM) to investigate the individual, synergistic, and antagonistic effects on Hexavalent chromium removal (Martino et al., 2015; Mourabet et al., 2017; Korbahti et al., 2008). Four factors were examined in the aqueous system: pH, contact time (hours), initial Hexavalent chromium concentration (mg/L), and TSB dosage (g/L). *Table 1* shows the experimental ranges of these factors. The symbols 0; ± 1; and ± α stand for the center, factorial, and axial points, respectively. In CCRD, α is a represents the distance between the center and axial points (Mourabet et al., 2017). In CCRD, α represents the distance between the center and axial points, calculated as $)^{1/4}$, where *k* is the number of experimental factors (Mourabet et al., 2017). Design Expert software was used for statistical experiment design (Mourabet et al., 2017; Korbahti and Rauf, 2008). The full matrix for the experimental model is presented in *Table 1*. Additionally, the quadratic equation model for determining the optimum conditions is presented as *equation (1)*:

$$\mathrm{A} = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k}\sum_{j=1}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ij} x_{ij}^2 + \varepsilon \quad (1)$$

where A as the response variable; β_0 as the intercept; β_i; β_{ij} are coefficients of the linear effect; double interactions; x_i; x_j: the independent variables; and ε: is error.

Table 1. *Experimental parameters for removing Hexavalent chromium from water using ascorbic acid treated sugarcane bagasse*

Factors	Unit	Levels				
		−α	−1	0	1	+α
A) pH		2	4	6	8	10
B) Contact time	hour	1	12.75	24.5	36.25	48
C) Initial Hexavalent chromium concentration	mg/L	50	62.5	75	87.5	100
D) Treated sugarcane bagasse (TSB)	g/L	0.5	0.875	1.25	1.625	2

Table 2. *The actual and predicted results in hexavalent chromium removal are based on the experimental design matrix and experimental parameters*

Run	Factors				Response	
	a) pH	B) contact time (hour)	C) Initial hexavalent chromium concentration (mg/L)	D) Adsorbent dosage (g/L)	Actual hexavalent chromium removal (%)	Predicted hexavalent chromium removal (%)
1	6	24.5	75	1.25	23.85	22.15
2	6	24.5	75	1.25	24.01	22.15
3	6	24.5	75	1.25	23.64	22.15
4	6	24.5	75	1.25	23.85	22.15
5	6	24.5	75	1.25	24.02	22.15
6	6	24.5	75	1.25	23.64	22.15
7	8	36.25	62.5	1.625	17.45	13.13
8	8	12.75	87.5	1.625	18.08	11.85
9	8	12.75	62.5	1.625	18.67	13.64
10	8	36.25	87.5	0.875	17.52	11.45
11	8	36.25	62.5	0.875	16.79	11.41
12	8	12.75	87.5	0.875	16.09	9.73
13	8	36.25	87.5	1.625	17.62	12.87
14	8	12.75	62.5	0.875	16.72	11.23
15	6	24.5	75	1.25	19.21	22.15
16	6	24.5	75	1.25	19.53	22.15
17	6	24.5	75	1.25	19.47	22.15
18	6	24.5	75	0.5	17.21	17.68
19	6	24.5	50	1.25	23.53	20.92
20	6	24.5	100	1.25	19.47	20.06
21	6	48	75	1.25	24.34	22.03
22	6	1	75	1.25	19.62	19.91
23	6	24.5	75	2	24.71	22.21
24	4	12.75	87.5	1.625	41.45	48.44
25	4	12.75	62.5	0.875	39.87	46.24
26	4	36.25	87.5	1.625	43.81	50.38
27	4	36.25	62.5	0.875	40.03	47.34
28	4	36.25	62.5	1.625	41.76	49.74
29	4	12.75	62.5	1.625	42.19	49.34
30	4	12.75	87.5	0.875	40.23	45.63
31	4	36.25	87.5	0.875	41.62	48.27
32	2	24.5	75	1.25	98.8	95.03
33	2	24.5	75	1.25	97.84	95.03
34	10	24.5	75	1.25	20.13	22.51
35	10	24.5	75	1.25	18.98	22.51

Adsorption experiments

Adsorption experiments were performed by adding a Hexavalent chromium solution to a 40 mL amber vial containing a predetermined amount of adsorbent. The vials were then placed in an incubator shaker set to 200 rpm for agitation. The residual concentrations of Hexavalent chromium were measured using a UV-vis spectrophotometer and the 1,5-diphenylcarbazide (DPC) method, calculated with the *equation (2)* (Labied et al., 2018):

$$\text{Hexavalent chromium Removal (\%)} = \frac{C_0 - C_i}{C^0} \times 100 \qquad (2)$$

where C_0 and C_i represent the initial and final concentrations of Hexavalent chromium, respectively. The equilibrium data obtained from the experiments were fitted to adsorption isotherms, including the Freundlich and Langmuir models. Kinetic data were analyzed using Pseudo-first-order and Pseudo-second-order models. To evaluate the accuracy of the model fitting, the regression model fits and the regression coefficients were determined.

Results and Discussion

FITR results

FTIR spectroscopy has been widely used for structural analysis of pretreated and chemically treated materials, as it provides direct information on changes in chemical functionalities. Specifically, before chemical treatment, O-H stretching is typically observed in the 3175–3490 cm^{-1} range (Demiral et al., 2008; Fan et al., 2017). Additionally, C-H and C-O stretching appear around 2850–2970 cm^{-1} and 1730 cm^{-1}, respectively (Al-Sulaimani et al., 2017; Cimino et al., 2013). The -COO vibration of acetyl groups is indicated by wavelengths between 1224–1236 cm^{-1} (Demiral et al., 2008; Hamadi et al., 2001; Phaenark et al., 2023; Srivastava et al., 2007; Yang et al., 2013). C-O-C stretching occurs in the 876–897 cm^{-1} range (Srivastava et al., 2007; Yang et al., 2013). Both pretreated and Hexavalent chromium-adsorbed sugarcane bagasse materials exhibit these common stretching functionalities. However, chemical treatment and Hexavalent chromium adsorption resulted in a reduction or elimination of certain functional groups (*Fig. 1*). Additionally, changes in the -COO functional group were observed, shifting from 1264 cm^{-1} to 1539 cm^{-1} in the Hexavalent chromium-adsorbed sugarcane bagasse material (Begmyrat and Ado, 2023).

SEM and SEM – EDX results

Fig. 2 displays the morphological characteristics of untreated and treated sugarcane bagasse, analyzed by SEM at 200μm magnification. In *Fig. 2a*, the untreated sugarcane bagasse shows a smooth surface with some debris, likely resulting from material sizing and physical impacts. However, after treatment with ascorbic acid, the sugarcane bagasse surface underwent significant changes. The structure became more irregular, with numerous voids and overlapping bagasse fibers. This altered morphology is advantageous for trapping and retaining contaminants within these cavities.

Fig. 1. *FTIR spectra of pretreated – treated – adsorbed Hexavalent chromium sugarcane bagasse*

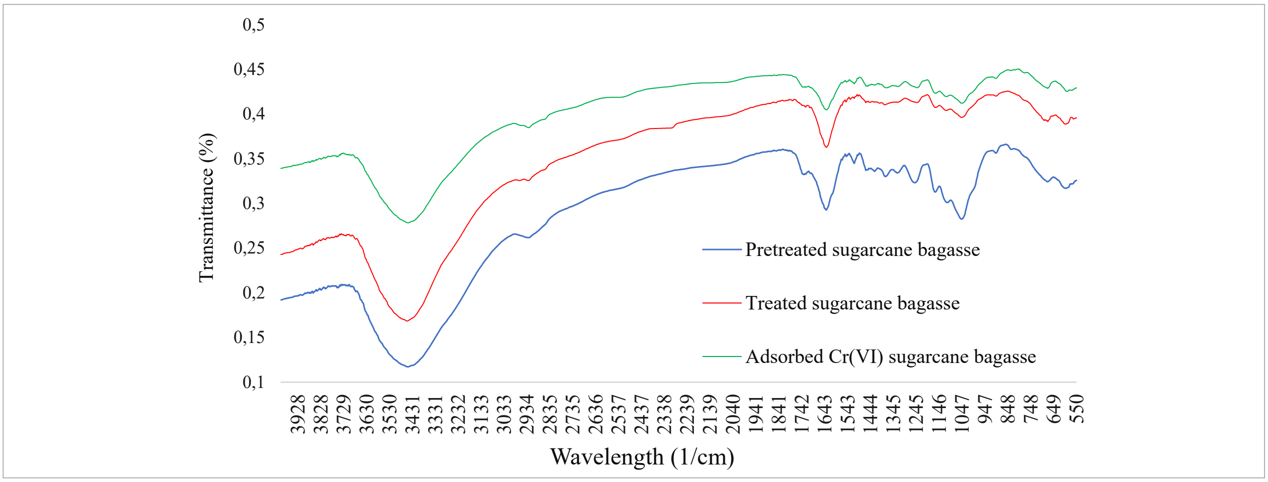
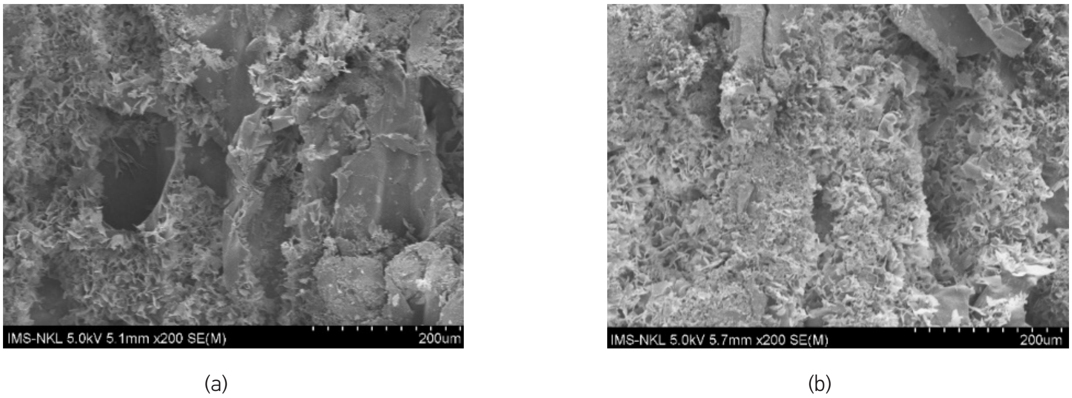


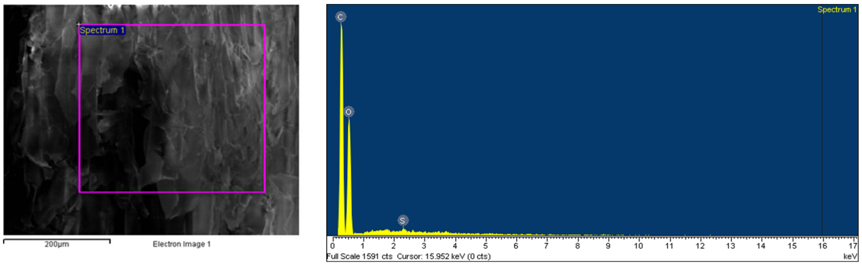
Fig. 2. *(a) SEM micrographs of raw sugarcane bagasse and (b) ascorbic acid treated sugarcane bagasse*



(a) (b)

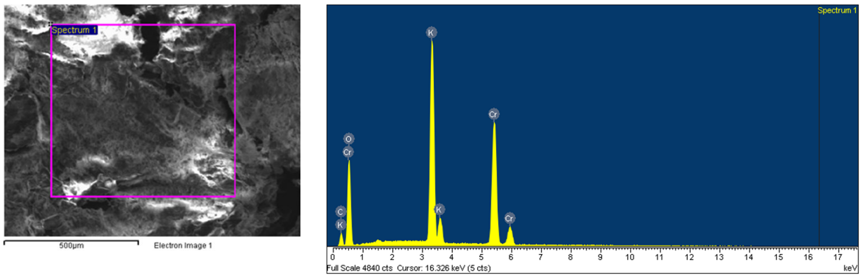
Fig. 3. *(a) SEM-EDX for raw sugarcane bagasse; (b) SEM – EDX results for Hexavalent chromium removal by TSB*

SEM – EDX results



Element	Weight (%)	Atomic (%)
C K	49.69	56.86
O K	50.12	43.06
S K	0.19	0.08
Totals	100.00	

(a)



Element	Weight (%)	Atomic (%)
C K	8.8	15.92
O K	46.00	62.44
K K	20.05	11.14
Cr K	25.15	10.51
Totals	100.00	

(b)

SEM – EDX results

SEM-EDX (Scanning Electron Microscope – Energy Dispersive X-ray) analysis enables rapid assessment of a sample's chemical composition, identifying both the elements present and their distribution. In this study, SEM-EDX analysis of the treated sugarcane bagasse (TSB) surface after Hexavalent chromium removal revealed the presence of chromium, alongside key biomass elements such as oxygen, potassium, and carbon (*Fig. 3*). Although the quantitative detection of chromium was moderate (Wt%: 25.15%; At%: 10.51%), this suggests that the TSB adsorbent may be an effective material for Hexavalent chromium removal.

The significant chromium weight percentage, despite a lower atomic percentage, may imply that chromium is present as a heavier compound, contributing more to the overall mass than to the atomic count. Compared with previous studies, this study achieved higher Hexavalent chromium adsorption through EDX analysis, outperforming results by Run and his team in 2022, who reported 0.3% Wt% Hexavalent chromium removal using Fe-modified biochar. However, our result (25.15% Wt%) was slightly lower than the 26% Wt% CrK observed in dormant spores of Aspergillus niger during Hexavalent chromium adsorption (Binqiao et al., 2018).

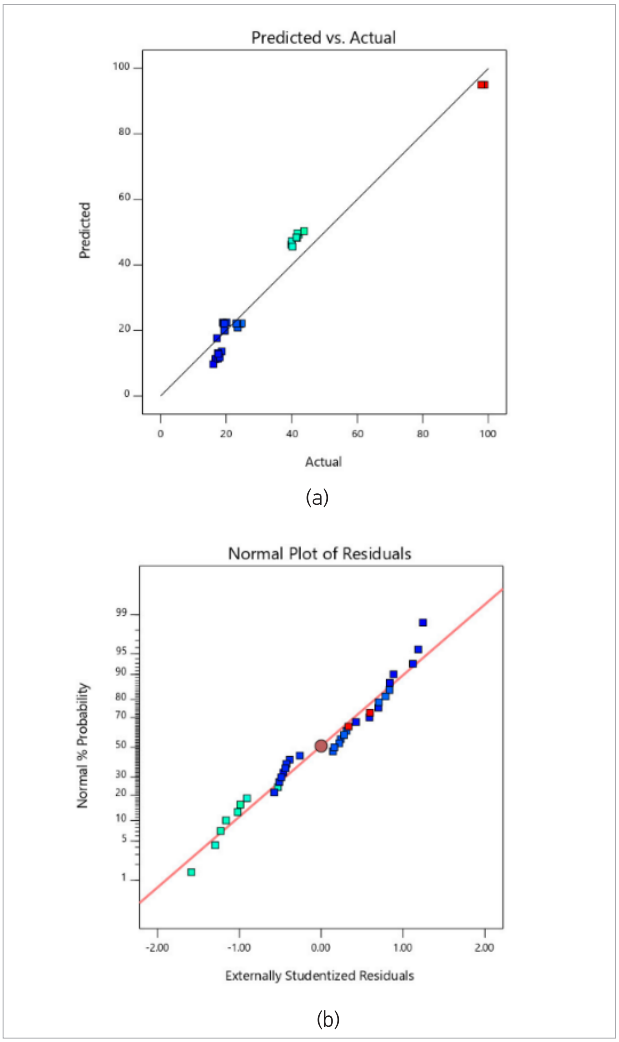
Developing, validating, and analyzing diagnostic models

Table 2 presents the experimentally observed Hexavalent chromium removal percentages at different pH levels, contact durations, initial Hexavalent chromium concentrations, and TSB dosages. The Hexavalent chromium removal efficiency ranged from 16.09% to 98.8% in experimental runs 12 and 32, respectively (*Table 2*). Both experiments were conducted at the same room temperature (25°C) but with varying initial Hexavalent chromium concentrations, TSB dosages, and pH conditions (8 and 2). Based on the experimental findings, an empirical model was developed to illustrate the relationship between Hexavalent chromium removal percentage and the influencing factors:

$$\begin{gathered}\text{Hexavalent chromium removal (\%)} = 22.15 - \\ 18.13a + 0.5308B - 0.2158C + 1.13D - \\ 0.2288aB - 0.2238aC - 0.1725aD + 0.3838BC - \\ 0.175BD - 0.0725CD + 9.15a^2 - 0.2956B^2 - \\ 0.4156C^2 - 0.5506D^2\end{gathered} \qquad (3)$$

The coefficients in the equation represent the linear, quadratic, and cubic terms of the components, respectively. A negative sign in the equation indicates an antagonistic effect, while a positive sign indicates a synergistic effect of a particular component (or combination of components) on the Hexavalent chromium removal percentage. The model's accuracy and suitability for representing the experimental data were assessed by plotting the experimental values against the predicted values from the RSM model (*Eq. 3*) (*Fig. 4a*). Additionally, the normal probability plot of residuals (*Fig. 4b*) served as a key diagnostic tool for identifying and interpreting any systematic deviations from the assumptions of normally distributed errors, independence of errors, and homogeneity of error variance. The high correlation coefficient ($R^2 = 0.9975$) demonstrated that the RSM model provided a close approximation of the actual Hexavalent chromium removal percentage, explaining 99.75% of the observed variance in the results. Furthermore, the close alignment between R^2 and the adjusted R^2 (adjusted. $R^2 = 0.9952$) confirmed the robustness of the model.

Fig. 4. *(a) Predicted and experimental plots for Hexavalent chromium elimination by ascorbic acid treated sugarcane bagasse; (b) the normal probability plot of residuals*



(a)

(b)

By using perturbation analysis, the impact of each variable on Hexavalent chromium adsorption by TSB was compared under optimal conditions (*Fig. 5*). The steep slope of the pH curve (a) indicates that pH plays a crucial role in Hexavalent chromium removal. *Table 3* shows the statistical verification of the model through analysis of variance (ANOVA). A *p*-value ≤ 0.05 indicates statistical significance for the model and its components at a confidence level above 99%. Conversely, a p-value exceeding 0.1 suggests that the model terms are not meaningful. In such cases, model reduction can improve the model by removing non-significant terms, except those necessary to maintain hierarchical structure. Furthermore, the regression model was used to generate 3D response surface plots (*Fig. 6*), which illustrate the relationship between variables and Hexavalent chromium adsorption capacity on TSB under the various conditions and treatment levels tested.

Fig. 5. *Perturbation plot of Hexavalent chromium adsorption onto TSB*

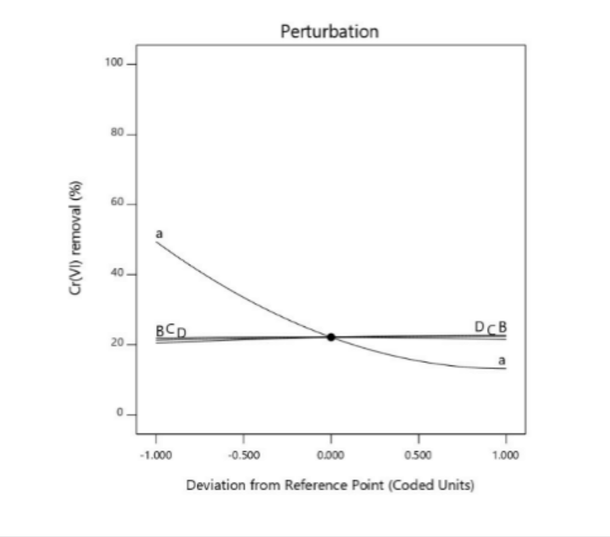
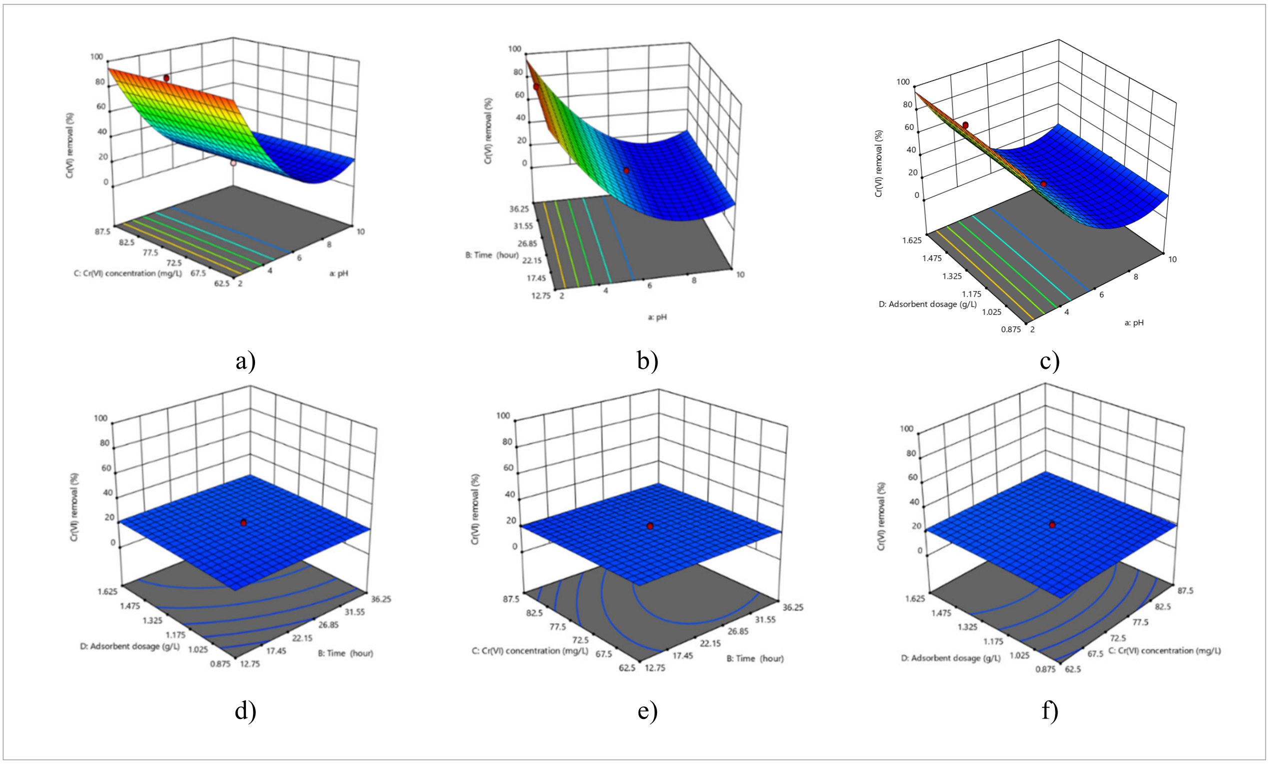


Table 3. *Analysis of variance of Hexavalent chromium removal by TSB*

Source of variation	Term df	Error df	F-value	p-value	
Whole plot	2	4.09	89.92	0.004	Significant
pH	1	4.09	120.05	0.004	
α^2	1	4.09	59.78	0.0014	
Subplot	12	13.82	2.68	0.0417	
B- contact time	1	16.02	4.91	0.0416	
C- Initial Hexavalent chromium concentration	1	16.02	0.8115	0.381	
D – Adsorbent dosage	1	16.02	22.3	0.0002	
aB	1	16.02	0.6077	0.4470	
aC	1	16.02	0.5814	0.4569	
aD	1	16.02	0.3456	0.5648	
BC	1	16.02	1.71	0.2094	
BD	1	16.02	0.3556	0.5593	
CD	1	16.02	0.0610	0.8080	
B^2	1	4.17	0.0617	0.8156	
C^2	1	4.17	0.1219	0.7439	
D^2	1	4.17	0.214	0.6667	
Standard error (group)	19.15	Mean	29.54	R^2	0.9975
Std.Dev	5.31	C.V %	17.97	Adjusted R^2	0.9952

Fig. 6. *Response surface plots showing the effect of independent variables on Hexavalent chromium adsorption onto TSB: a) Hexavalent chromium concentration and pH; b) contact time and pH; c) Adsorbent dosage and pH; d) Adsorbent dosage and contact time; e) Hexavalent chromium concentration and contact time; f) adsorbent dosage and Hexavalent chromium concentration on Hexavalent chromium adsorption*



a) b) c) d) e) f)

Effects of variables on Hexavalent chromium adsorption pH effects on Hexavalent chromium removal

It is widely recognized that pH significantly influences pollutant removal processes. Consequently, an experiment was conducted with an initial Hexavalent chromium concentration of 100 ppm, a TSB dosage of 0.5 g/L, and a stirring speed of 70 rpm to investigate the effect of pH on Hexavalent chromium removal. The study found that as pH increased, Hexavalent chromium adsorption decreased (*Fig. 7*). Along with the adsorbent's surface charge, the pH solution influences the speciation of metal ions. Hexavalent chromium primarily occurs as chromic acid (H_2CrO_4) at pH < 2. Chromate (CrO_4^-) is the only ion that predominates above pH 7, while hydrogen chromate ($HCrO_4^-$) is dominant at pH 2–7. Prominent monovalent hydrogen chromate ($HCrO_4^-$) gradually converts to divalent chromate (CrO_4^-; $Cr_2O_7^{2-}$) ions, which explains the steady decrease in adsorption from acidic to neutral pH (Haroon et al., 2017). Compared to monovalent ions, divalent ions absorbed less frequently on TSB because of their larger free energy of adsorption. The aqueous solution around the TSB also experienced deprotonation on its surface, which resulted in a reduction of positive surface charges. This led to lower chromate ion adsorption as pH increased because the negatively charged chromate ions encountered electrostatic repulsion at higher pH levels.

Fig. 7. *Effect of pH on Hexavalent chromium removal by TSB*

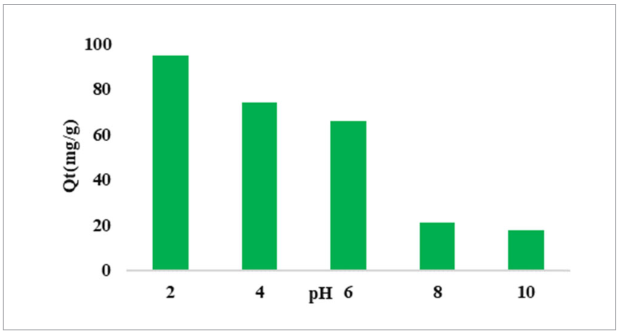
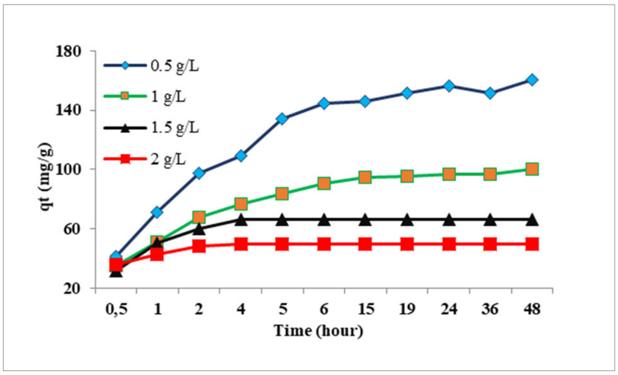


Fig. 8 shows the effect of contact time and TSB dosage concentration on hexavalent chromium removal. During a few early hours, the Hexavalent chromium efficient removal was dramatically lifted from 20 mg/g to 98 mg/g with 0.5 TSB dosage concentration (*Fig. 8*) under the initial Hexavalent chromium concentration 100mg/L in 40 mL; contact time from 0.5 to 48 hours; TSB dosage concentration from 0.5 to 2 g/L; stirring speed: 70 rpm; pH 2. From 2 to 48 hours, Hexavalent chromium removal was continuously increased with 0.5 g/L TSB. For higher TSB dosage concentration, the Hexavalent chromium efficient removal was slightly increased and slowly reached the equilibrium statement.

Fig. 8. *Hexavalent chromium removal by ascorbic acid-treated sugarcane bagasse under various dosage concentrations*



Kinetic and isotherm adsorption study

Kinetic and isotherm studies are important in determining the adsorption mechanism for any heavy metal removal. Hence, in the study we investigated some core kinetic and isotherm models including Pseudo-first and second orders; Langmuir; and Freundlich models. The mathematical expressions are described in *equation (4)*; *(5)*; *(6)*; and *(7)* (Begmyrat and Ado, 2023).

Pseudo-first order: $$\text{Log}\,(q_e - q_t) = \text{Log}q_e - \frac{K_1 t}{2.303} \quad (4)$$

Pseudo-second order: $$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Langmuir: $$\frac{C_e}{q_e} = \frac{1}{q_{max}}\frac{1}{K_L} + \frac{1}{q_{max}}C_e \quad (6)$$

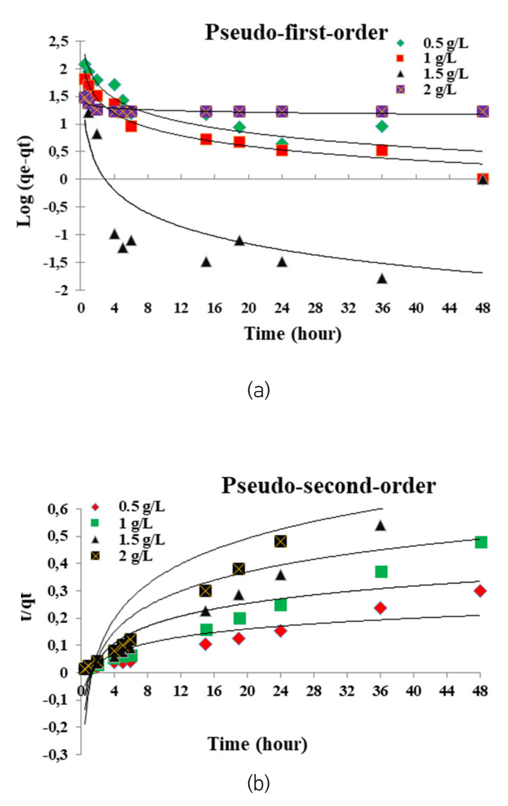
Freundlich: $$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (7)$$

where q_{max}: is the optimal adsorption capacity (mg/g); K_L is the Langmuir constant (L/mg); K_f: is the adsorption capacity; n is the adsorption intensity; K_1 and K_2 are the rate constant for the Pseudo first and second order (g/mg.h); q_t and q_e are the amount of adsorption capacity at time t and equilibrium time (mg/g), respectively. C_e is a concentration at equilibrium time (Majeed et al., 2014; Srivastava et al., 2007; Martino et al., 2015).

Kinetic study results

The results of the kinetic study are presented in *Fig. 9* and *Table 4*. The pseudo-first-order kinetic model did not fit the experimental data well. In contrast, the pseudo-second-order kinetic model showed a favorable fit, as evidenced by the kinetic parameters listed in *Table 4*. The high regression coefficient value suggests that the pseudo-second-order model accurately represents the data. This model also provided a reasonable estimation of the experimental equilibrium adsorption capacity. Based on these findings, we propose that Hexavalent chromium adsorption onto TSB is a physisorption process, with the adsorption rate being proportional to the availability of adsorption sites.

Fig. 9. *Adsorption kinetic studies for the removal of Hexavalent chromium by ascorbic acid treated sugarcane bagasse: (a) Pseudo – first – order; (b) Pseudo – second – order*



(a)

(b)

Table 4. *Pseudo–first order and Pseudo – second order results for various TSB dosage concentrations*

Pseudo–first order				
0.5 g/L	$R^2 = 0.2141$	Unfavorable		
1 g/L	$R^2 = 0.8299$	Unfavorable		
1.5 g/L	$R^2 = 0.846$	Unfavorable		
2 g/L	$R^2 = 0.1562$	Unfavorable		
Pseudo–second order				
0.5 g/L	$R^2 = 0.9987$	Favorable	$K_2 = 0.0045$	$Q_e = 161.29$ mg/g
1 g/L	$R^2 = 0.9997$	Favorable	$K_2 = 0.0097$	$Q_e = 101.01$ mg/g
1.5 g/L	$R^2 = 0.9999$	Favorable	$K_2 = 0.07655$	$Q_e = 67.11$ mg/g
2 g/L	$R^2 = 1$	Favorable	$K_2 = 0.266$	$Q_e = 50$ mg/g

Isotherm study results

The Langmuir and Freundlich models are widely recognized as primary adsorption isotherm models. These models were applied to the experimental data and are presented in *Fig. 10* and *Table 5*. The relationship between $1/q_e$ and $1/C_e$ for Hexavalent chromium adsorption onto TSB is described by *Eq. (6)*. The slope and intercept of the Langmuir equation were used to determine the values of K_L and q_{max}. The Langmuir model demonstrated a strong fit for this study, with a maximum adsorption capacity of 162 mg/g and a high correlation coefficient $R^2 = 1$. This suggests monolayer adsorption, as proposed by the Langmuir model, and indicates that the adsorption of Hexavalent chromium on TSB is "favorable" according to the computed separation factor. Conversely, the Freundlich model, which can be linearized by plotting Log q_e against Log C_e (*Fig. 10*), did not align well with the experimental data, as indicated by a lower R^2 ($R^2 = 0.6583$) (*Table 5*).

Table 5. *Isotherm model results*

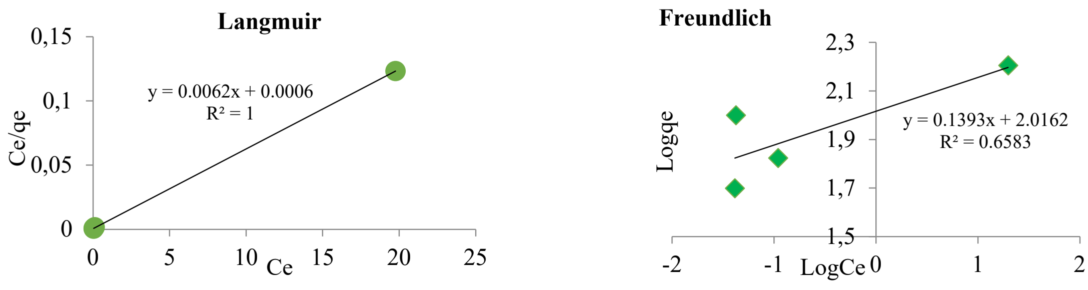
Langmuir	$R^2 = 1$	$q_{max} = 162$ mg/g	$K_L = 10.33$
Freundlich	$R^2 = 0.658$	$n = 7.187$	$K_f = 103.8$

In comparison to literature references, the Hexavalent chromium adsorption capacity observed in this study exceeds that of activated carbon from olive bagasse, dormant spores of Aspergillus niger, rice husk modified with sorbic acid, sawdust, and tire-based adsorbents (*Table 6*). While the results are not exceptionally higher than those in previous studies, this material demonstrates an improvement in Hexavalent chromium removal from water. This study serves as a foundation and shows potential for further enhancing the material's effectiveness and exploring its ability to remove other multi-metal ions from water supplies and wastewater.

Table 6. *Comparison sugarcane bagasse modified by ascorbic acid with other previous relevant studies*

Adsorbent	pH	Adsorption capacity	Reference
Dormant spores of aspergillus niger	2	97.19 mg/g	Binqiao et al., 2018
Activated carbon from olive bagasse	2	88.59 mg/g	Demiral et al., 2008
Rice husk modified by sorbic acid	2	97.09 mg/g	Huong and Trang, 2023
Sawdust	2	37.785 mg/g	Hamadi et al., 2001
Tyres	2	48.19 mg/g	Hamadi et al., 2001
This study	2	162 mg/g	This study

Fig. 10. *(a) Langmuir isotherm result; (b) Freundlich isotherm result*



(a)

(b)

Conclusions

Biosorption has emerged as an effective and environmentally friendly approach for removing harmful metals, such as hexavalent chromium (Hexavalent chromium), from aqueous matrices. This study proposes the use of sugarcane bagasse (TSB), modified with ascorbic acid, as an adsorbent for Hexavalent chromium removal from water. To gain insight into the morphology and chemical interactions of TSB with Hexavalent chromium, FTIR and Scanning Electron Microscopy – Energy Dispersive X-ray (SEM-EDX) analyses were conducted. Key functional groups, including O-H, C-O-C, and -COO, were identified as significantly beneficial for Hexavalent chromium removal. Additionally, the TSB adsorbent's rough surface, as revealed by SEM analysis, was well-suited for trapping heavy metals within numerous microscopic pores. SEM-EDX analysis further confirmed the presence of chromium on the TSB surface following adsorption experiments. The optimization of Hexavalent chromium removal from aqueous environments was achieved using response surface methodology (RSM) and statistical experimental design. An empirical model was developed and statistically validated to describe the effects of pH, initial Hexavalent chromium concentration, contact time, and adsorbent dosage on Hexavalent chromium removal efficiency. Among these variables, pH exerted the most significant control over adsorption performance. The RSM model predicted a Hexavalent chromium removal rate of 99%, which was subsequently confirmed through experimentation. Kinetic and isotherm studies indicated that optimal conditions for Hexavalent chromium removal were achieved at pH 2–3, with a contact time of 15 hours and an initial Hexavalent chromium concentration of 100 ppm. Analysis using the Langmuir model yielded a high correlation (R^2 = 1), ndicating a maximum Hexavalent chromium adsorption capacity of 162 mg/g for TSB. Additionally, the pseudo-second-order model showed strong alignment with the experimental data, suggesting that the adsorption process is well-represented by this kinetic model.

{Gurauskiene, 2006, Eco-design methodology for electrical and electronic equipment industry}

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Supplementary data

Material treatment processing: