

Chromium adsorption using powdered leaves of *Prosopis cineraria*: Kinetic, isotherm, and optimization by response surface methodology

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ABSTRACT

In this study, the effectiveness of *Prosopis cineraria* leaves powder in removing chromium from an aqueous solution was examined. The test was done in batch mode and the effect of *Prosopis cineraria* doses (1–5 g/L), initial pH (1.5–3.5), initial concentrations of chromium (10–50 mg/L), and contact times (15–75 min) on the biosorption process was examined. The results of response surface methodology indicated that under the best operating conditions with *Prosopis cineraria* dose of 3.98 g/L, initial chromium concentration of 25.41 mg/L, contact time of 59.82 min and pH of 2.02, chromium removal efficiency was selected as a maximum value of 89.65%. The adsorption aligns with the Langmuir isotherm and pseudo-first-order kinetic models. The maximum adsorption capacity for chromium was determined to be 55.55 mg/g, indicating the high efficacy of *Prosopis cineraria* in removing chromium ions. The findings suggest that *Prosopis cineraria* leaves powder could be a cost effective alternative to more expensive heavy metal adsorbents from aqueous solution, but notes more research is needed on the efficiency of *Prosopis cineraria* for industrial wastewater. Future studies should focus on SEM, XRD and FTIR analysis to enhance understanding of the adsorption mechanisms and potential applications for chromium removal.

1. Introduction

Human activities and industrial processes have led to the release of harmful heavy metals like chromium into water bodies, posing a serious threat to human health and ecosystems [1]. Chromium, especially in the form of hexavalent chromium [Cr(VI)], is highly toxic and can cause cancer. High levels of chromium in water can harm aquatic organisms and human health [2]. It can accumulate in sediment and water, entering the food chain and causing adverse effects on biological systems. Chronic exposure to elevated levels of chromium in humans can lead to severe health issues, including dermatitis, respiratory problems, and cancer [3]. Effective remediation strategies are crucial to address the environmental and health concerns associated with chromium contamination. The World Health Organization (WHO) has recognized the carcinogenic and toxic effects of hexavalent chromium on humans. Recommended maximum levels for total chromium in drinking water are 0.05 mg/L [4]. The permitted limits for discharge to surface water are 0.1 mg/L in the United States and the European Union [5]. The concentration of chromium in industrial effluent is usually in the range of 50–200 mg/L [6,7].

Various techniques have been used to reduce heavy metal toxicity in water, including membrane processes, electrochemistry, electro dialysis, advanced oxidation and adsorption. However, these methods have drawbacks such as time consumption, high energy usage, waste production, toxic by-product formation, low water flux, and membrane fouling. Among them, adsorption process where adsorbent materials adhere to a surface using physical forces. The effectiveness of the process is influenced by various factors including the textural properties of the adsorbent, the pH of the solution, the amount of adsorbent used, temperature, and the presence of competing adsorbate in the medium. Some of the benefits of adsorption include its simple operational design, the ability to desorb the adsorbate, and the potential for reusing the adsorbent, which has led to continuous research interest in this technique within the scientific community [8–10].

Over the past few years, there has been a growing interest in using natural adsorbents, especially plant-based materials, as a cost-effective and environmentally friendly approach to remove heavy metals from water solutions. *Prosopis cineraria*, which belongs to the Fabaceae family, is a small tree that is 3 to 5 m high. An important economical

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species that grows in arid and semi-arid regions of India, Afghanistan, Pakistan, Iran and Saudi Arabia [11,12]. In Iran, *Prosopis cineraria* trees grow in coastal areas of Khuzestan, especially in the cities of Abadan and Khorramshahr. Due to its abundance, low cost and safe for human health, the leaves of these trees can be used as biosorbents easily. *Prosopis cineraria* has shown potential for water treatment by effectively eliminating heavy metal pollutants like chromium, lead, and cadmium from water solutions [13–15]. The presence of bioactive compounds such as tannins, flavonoids, and alkaloids in powdered leaves of *Prosopis cineraria* has proven to be promising in adsorbing heavy metals. The unique surface properties and chemical composition of *Prosopis cineraria* enable it to effectively absorb heavy metals, especially chromium, through processes like ion exchange, surface complexation, and electrostatic interactions. Research has also demonstrated its high effectiveness in removing lead and cadmium from water sources. These findings support the suitability of *Prosopis cineraria* for water remediation efforts and environmental sustainability [16].

The traditional and standard approaches for determining the best level are extremely time-consuming and involve numerous experiments, making them unreliable. Response surface methodology (RSM) utilizes an experimental design that systematically reduces the number of experiments and examines multiple R^2 evaluations to identify conditions that result in the most suitable response within the experimental range. RSM is a valuable approach for concurrently assessing the relationship between the impacts of various individual parameters. In numerous research studies, response surface methodology is used to optimize heavy metals removal using bioadsorptions [17,18]. For instance, Khoshraftar et al. [17] applied RSM to heavy metals elimination using dolomite powder. The results of central composite design (CCD) showed that the maximum adsorption of heavy metals was 60 mg/L and 293 K with a desirability of 0.976. Another study confirmed that the efficiency for removal of As, Cd, Co, Cr and Fe with a high coefficient of R^2 (99%) using *Chlorella colonialis* under RSM was more than 95% [19]. Isam et al. found that biosorption onto *Gracilaria changii* using RSM showed the maximum removal percentages of Pb(II) and Cu(II) were 96.3% and 44.77%, respectively [20]. Bayuo et al. optimized biosorption of hexavalent chromium using RSM from aqueous media. The results revealed that the maximum adsorption capacity was achieved 2.355 mg/g when the contact time, pH, initial Cr(VI) concentration were 120 min, 8.0, and 50 mg/L [21].

Despite various techniques employed for heavy metal removal, there is a need for sustainable and cost-effective approaches. The novelty of this research lies in the utilization of *Prosopis cineraria*, a readily available plant material, for chromium remediation. By exploring the potential of a readily available, natural adsorbent material, this work seeks to offer a sustainable and cost-effective solution for chromium remediation from industrial wastewater in the semi-arid region of Iran. This study aims to elucidate the adsorption mechanism and kinetics of chromium removal onto *Prosopis cineraria* leaf powder, providing insights into the potential applicability of this natural adsorbent for real-world environmental remediation efforts. Moreover, the performance of the bioadsorption process in terms of chromium removal was optimized using Response Surface Methodology (RSM) and Central Composite Design (CCD) to determine the impact of key variables.

2. Materials and methods

2.1. Preparing adsorbent

After collecting Leaves of *Prosopis cineraria*, the samples were transferred to the pilot laboratory of the Faculty of Health. The leaves were thoroughly washed with distilled water to eliminate any dust or soluble impurities, and then left to dry at room temperature (25–30 °C). Subsequently, the leaves were placed in an oven at 105 °C for 6 h, crushed using 0.71 mm plate and then sieved. Each experiment was conducted twice times. The mean values of the outcomes are discussed in this study. Chromium adsorption capacity and efficiency [22]:

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

$$R_e(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where q is the adsorption capacity (mg/g) of C_i , C_0 , and C_e , respectively, are initial, final concentration, and equilibrium of chromium solution (mL), V is the sample volume in liter and W is the total amount of adsorbent (g). C_0 and C_t are the initial and final concentrations of the pollutants, respectively.

2.2. Preparation of Cr (VI) solutions

The impact of different doses of biosorbent (1, 2, 3, 4, and 5 g/L), initial pH (1.5, 2, 2.5, 3, and 3.5), initial concentrations of chromium (10, 20, 30, 40, and 50 mg/L), and contact times (15, 30, 45, 60, and 75 min). To prepare a stock solution of Cr (VI), 2.8287 g of 99.9% potassium dichromate ($K_2Cr_2O_7$) was dissolved in 1000 mL of water. This stock solution was then diluted as needed to create standard solutions with concentrations ranging from 10–50 mg/L of Cr (VI). The pH of the solution was adjusted using either 0.5 N HNO_3 or 0.5 N $NaOH$ solutions, as required, and was measured using a pH meter (CONSORT C831 Belgium).

In each experiment, a 100 mL solution containing a specific initial chromium concentration and known amounts of *Prosopis cineraria* was poured into a 500 mL flask containing 0.14 g of potassium dichromate. The mass of each adsorbent was calculated based on a volume of 100 cc, which is equivalent to 0.1 g per liter. The solution was transferred to a stirrer (POLE IDEAL PARS Iran) and set at a speed of 180 rpm for a specified time. After stirring, the solutions were filtered using a 0.42 μ -Whatman filter paper (UK filter paper size 12.5 cm). The filtrates were collected and analyzed the concentration of chromium using atomic absorption spectrophotometer (BRAIC wfx-130 AA Spectrophotometer). The obtained values were used to determine the adsorption isotherm and kinetic equation.

2.3. Response surface methodology

Compared to other modeling approaches [23], Response Surface Methodology (RSM) and Central Composite Design (CCD) are effective statistical techniques for modeling and optimizing the simultaneous impacts of important parameters within a four-factor, five-level framework [24]. These five levels are classified as two axial points, two factorial points, and one central point for each variable. In this study, these two statistical tools were utilized to model and optimize the effects of four crucial variables, namely biosorbent (1, 2, 3, 4, and 5 g/L), pH (1.5, 2, 2.5, 3, and 3.5), initial concentrations of chromium (10, 20, 30, 40, and 50 mg/L), and contact times (15, 30, 45, 60, and 75 min), on the performance of the biosorption *Prosopis cineraria* in terms of chromium removal efficiency. The four variables are coded as presented in Table 1, with $-\alpha$ and $+\alpha$ representing the extreme levels for each variable.

Factorial designs are limited in their ability to predict curvature or critical points in the designed space. Therefore, RSM was employed to model the process with fewer experimental runs and a more precise analysis of the variables in various formats [25]. The specific number of experiments is determined based on the number of variables using the following equation:

$$E = 2^v + 2V + P \quad (3)$$

where E is the number of demanded experiments for analysis, V is the number of independent variables, and P is the number of replications at the central point. The empirical model used was a second-order polynomial regression, represented by Eq. (4), which helped in analyzing the interaction between the dependent variable (Y) and the independent variables.

Table 1
The coded levels and range of the studied variables.

Variables	Unit	Type	Coded levels				
			- α	-1	0	+ 1	+ α
Adsorbent dose	g/L	A	1	2	3	4	5
Initial chromium concentration	mg/L	C	10	20	30	40	50
Time	min	D	15	30	45	60	75
pH	-	B	1.5	2	2.5	3	3.5

$$Y = \beta_0 + \sum_{i=1}^{i=k} \beta_i x_i + \sum_{i=1}^{i=k} \beta_{ii} x_i^2 + \sum_{1 \leq i < j}^{i=k} \beta_{ij} x_i x_j + \varepsilon \tag{4}$$

where Y denotes the result (removal efficiency of chromium in percentage), j is second-order, i is the linear constant, β₀ is a constant coefficient, β_i is the regression constant, β_{ii} is the quadratic coefficient, β_{ij} is the interaction coefficient and ε is a random error. Also, x_i and x_j are the coded independent variables. The process of the whole methodology is shown in Fig. 1.

3. Results and discussions

3.1. Statistical analysis and model fitting via central composite design

Following the utilization of the five-level coding system illustrated in Table 2, the CCD method was utilized to evaluate the impact of the variables on chromium removal through *Prosopis cineraria* biosorption. The replication of central points for each variable was conducted to identify model errors and assess the final regression quality. Out of 30 experimental runs, 24 were designed at factorial and axial points, while the remaining runs (#26, #27, #28, #29, and #30) were replicated at the central point (3 g/L, 30 mg/L, 45 min, and 2.5). As shown in Table 2, Cr removal varied between about 31% and 88%.

3.2. Modeling and data analysis

The second-order polynomial functions were used to fit the predicted values, with Y representing Cr removal (%). The parameters A, B, C, and D correspond to the *Prosopis cineraria* dose, initial chromium concentration, time, pH, respectively, as shown in Eq. (5).

$$Y \text{ (Cr removal efficiency, \%)} = 69.71 + 5.99A + 6.20B + 5.72C - 8.56D - 4.09AB + 2.56AC - 5.17BC - 1.68BD - 3.25CD - 3.07A^2 - 3.67B^2 - 1.14C^2 - 1.47D^2 \tag{5}$$

To assess the suitability of the model, an analysis of variance (ANOVA) was conducted, as shown in Table 3. The statistically significant results (p < 0.0001) for Cr removal in relation to the model's terms listed in Table 3. In this context, terms A, B, C, and D had significant effects on Cr removal efficiency. According to the result, the quadratic equations A², B², C² and D², as well as the coefficients of AB, AC, BC, BD, CD had significant effects on Cr removal efficiency. Relatively high values of R² and Adj.R² were equal to 98% and 96%, respectively, which confirms the correlation coefficients of the quadratic equation. Relatively high values of R² indicate the accuracy of the quadratic equation for *Prosopis cineraria* dose, initial chromium concentration, time, and pH.

Fig. 2a and b shows the probability of being normal the residues of each response and that the experiments are random. A diagram will show the normal probability of residuals if the points are on a straight line, which shows the normal distribution of residues. The normal probability diagram of the residues indicates the degree that the chromium removal residues follow the normal distribution. Furthermore, Fig. 2(b) indicates the being randomized the experiments. In terms of model accuracy, the points should follow roughly a diagonal line, as shown. This confirms the model's suitability for Cr removal efficiency.

3.3. Interaction of variables on chromium removal by *Prosopis cineraria*

The combined effectiveness of key factors, including *Prosopis cineraria* dose, initial chromium concentration, time, and pH duration on the removal of Cr efficiency were assessed, optimized by mathematical models RSM and CCD. Fig. 3 shows the interactions of independent variables including initial chromium concentration, and *Prosopis cineraria* adsorbent dose on Cr removal. As shown in Fig. 3(a) the highest chromium removal rate (more than 72%) occurred by *Prosopis cineraria* adsorbent at initial concentration of 3500 mg/L and adsorbent dose of 3.5 g/L. The chromium removal efficiency decreases as the initial

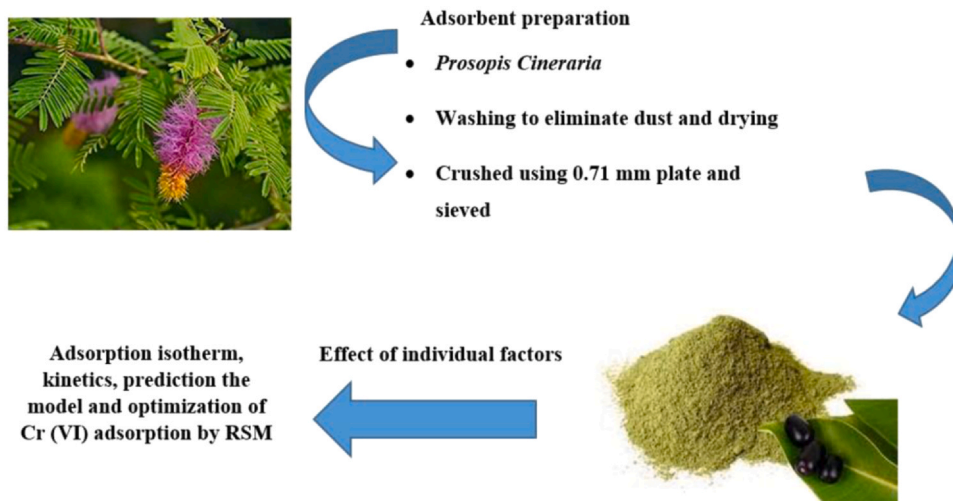


Fig. 1. General methodology of the study.

Table 2
CCD experimental design and the response results for chromium removal using *Prosopis cineraria* absorption.

Run	Adsorbent dose (g/L)	Initial chromium concentration (mg/L)	Time (min)	pH	Response Chromium Removal (%)	
					Predicted	Actual
1	2	20	30	2	40.35	42.45
2	4	20	30	2	53.43	54.52
3	2	40	30	2	74.64	75.65
4	4	40	30	2	71.34	72.55
5	2	20	60	2	63.52	64.34
6	4	20	60	2	86.83	88.45
7	2	40	60	2	77.11	78.32
8	4	40	60	2	84.05	85.45
9	2	20	30	3	31.10	31.22
10	2	20	30	3	48.12	47.41
11	4	40	30	3	58.68	57.56
12	2	40	30	3	59.33	60
13	4	20	60	3	41.27	40.56
14	2	20	60	3	68.52	69
15	2	40	60	3	48.16	48.56
16	4	40	60	3	59.05	57.45
17	1	30	45	2.5	45.46	44.54
18	5	30	45	2.5	69.42	68.34
19	3	10	45	2.5	42.64	41.23
20	3	50	45	2.5	67.45	66.87
21	3	30	15	2.5	53.71	52.52
22	3	30	75	2.5	76.59	75.78
23	3	30	45	1.5	80.88	76.65
24	3	30	45	3.5	46.62	48.85
25	3	30	45	2.5	69.71	71.56
26	3	30	45	2.5	69.71	68.79
27	3	30	45	2.5	69.71	64.13
28	3	30	45	2.5	69.71	70.11
29	3	30	45	2.5	69.71	75.13
30	3	30	45	2.5	69.71	68.54

Table 3
ANOVA results of experiment data for Cr removal using *Prosopis cineraria*.

Source of variations	Sum of Squares	df	Mean square	F-Value	Prob > F	Remarks	
Model	5923.24	14	423.09	54.73	< 0.0001	Highly significant	
A- <i>Prosopis cineraria</i> dose	861.00	1	861.00	111.39	< 0.0001	Highly significant	
B- initial chromium concentration	923.18	1	923.18	119.43	< 0.0001	Highly significant	
C- Time	785.13	1	785.13	101.57	< 0.0001	Highly significant	
D- pH	1760.45	1	1760.45	227.75	< 0.0001	Highly significant	
AB	267.90	1	267.90	34.66	< 0.0001	Highly significant	
AC	104.81	1	104.81	13.56	< 0.0022	significant	
AD	15.54	1	15.54	2.01	0.1766		
BC	427.97	1	427.97	55.37	< 0.0001	Highly significant	
BD	44.92	1	44.92	5.81	0.0292	significant	
CD	168.94	1	168.94	21.86	0.0003	significant	
A ²	256.25	1	256.25	33.41	< 0.0001	Highly significant	
B ²	368.62	1	368.62	47.69	< 0.0001	Highly significant	
C ²	35.70	1	35.70	4.62	0.0483	significant	
D ²	60.97	1	60.97	7.89	0.0132	significant	
Residual	115.95	15	7.73				
Lack of Fit	49.64	10	4.96	0.37	0.9127		
Pure Error	66.31	5	13.26				
Cor Total	6039.19	29					
PRESS	AP	Pred.R ²	Adj.R ²	R ²	CV	Mean	SD
381.39	28.34	0.94	0.96	0.98	4.47	62.22	2.78

chromium concentration and adsorbent dose decrease. As the adsorbent dose was gradually reduced to below 2 g/L, the removal of Cr decreased by 50% during treatment time. Devaprasath et al. [26] achieved that Cr removal decreased by increasing adsorbent dose, which was in contrast with the present study. This phenomenon can be described as that with a fixed adsorbent dose, the total available adsorption sites remain constant for all the concentrations [27]. Therefore, Cr removal rate has demonstrated a significant decrease as the initial chromium concentrations increase. However, in another study carried out by Eshraghi et al. [28] regarding the elimination of cadmium by *Prosopis cineraria*, it

was found that the rate of cadmium removal increased as the adsorbent dose increased, aligning with the findings of the current study. Shahmaleki et al. [29] also obtained comparable findings in their research, showing that the rate of lead removal increased with higher doses of the adsorbent.

Recent studies on the impact of reaction time on the elimination of heavy metal ions shows that the rate of adsorption is typically high during the initial phase of adsorption processes [30]. Fig. 3(b) indicates that the highest Cr removal efficiency of 85% was achieved by increasing the adsorbent dose to approximately 5 g/L and extending the

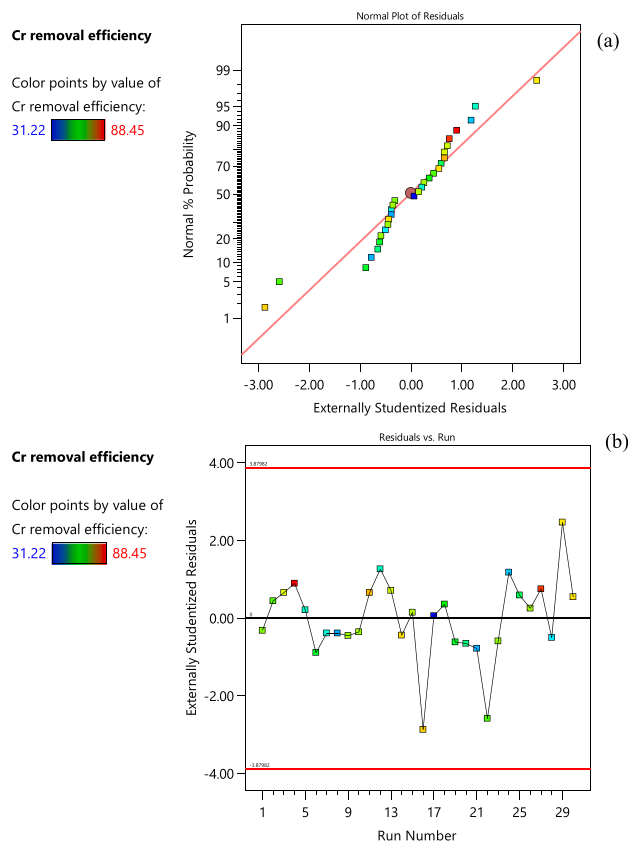


Fig. 2. (a) Distribution diagram of the normal probability of residues and (b) random of experiments in Cr removal by *Prosopis cineraria*.

reaction time to 75 min. Study suggests that as the contact time increases, the percentage of removal also increases. This is because the active and vacant sites on the adsorbent surface become occupied over time, leading to a higher rate of adsorption initially and a decrease in adsorption capacity over time. Therefore, the amount of adsorption decreases in the later stages. Hence, the minimum and maximum Cr removal rates were below 50% in 10 min with 1 g/L of *Prosopis cineraria* dose and 85% in 75 min with 50 g/L of *Prosopis cineraria* dose, respectively. Based on the two-dimensional graph, the optimal removal rate was 75% in 50 min and the adsorbent dose is 4 g/L, and since then, no significant increase in the removal rate has been reported. Study found that with increasing contact time, the amount and percentage of chromium removal increases. The findings revealed that the highest amount of Cr removal was 94.36% in 120 min [27].

Fig. 4 shows the interaction diagram of independent variables including initial chromium concentration, pH and reaction time on Cr removal. Fig. 4(a) shows the interaction between initial chromium concentration and reaction time on Cr removal. At this stage, different chromium concentrations (10, 20, 30, 40, 50 mg/L) were added to the chromium solution at 3 g/L *Prosopis cineraria*. As can be seen, the highest removal of chromium (75%) from aqueous solution was obtained at a time above 60 min and the concentration of Cr range from 15–35 g/L. By decreasing the concentration of Cr and reducing the reaction time, the removal efficiency dropped to below 40%. In a water-based solution, a force is created with the initial concentration of sorbate, which helps to move Cr (VI) ions onto the surface of the adsorbent [31]. Therefore, the impact of the initial concentration of Cr (VI) is also an important factor. In the same vein, with increasing the initial chromium concentration, the removal efficiency has also increased up to 75% with Cr concentration of 35 mg/L in 65 min, after which there is a decrease in efficiency. This phenomenon can be explained by the fact that as the initial concentration of chromium increases, the available

adsorption sites on the adsorbent surface become occupied, resulting in a decrease in removal efficiency [32].

The surface charge of the biosorbent can be altered by the pH, and it can also impact the level of ionization and speciation of the heavy metal in the solution [33]. At this stage, different chromium concentrations (1.5, 2, 2.5, 3, 3.5) were added to the chromium solution at 3 g/L *Prosopis cineraria*. In Fig. 4(b), the highest removal efficiency of Cr using *Prosopis cineraria* was observed at acidic pH and when the initial concentration of Cr ranged from 35–50 mg/L. While as the pH increases beyond 3, the efficiency of chromium removal gradually decreases to below 40%. At acidic pH levels, the H^+ ions competed with the chromium ions for the available sites on the surface of *Prosopis cineraria*. This is because the concentration of H^+ ions in an aqueous medium was reported to be high. As the pH increased, the concentration of H^+ ions decreased, leading to a decrease in competition for the sites [34]. Shahmaleki et al. [29] observed that high removal of lead (90%) achieved at pH 6 using nano *Prosopis cineraria* leaf ash and as pH went up from 6 to 10, the removal efficiency decreased. The results of the study of Devaprasath et al. [26] also emphasized on increasing the removal efficiency of chromium at low pH, especially at pH 2. Contrast to these findings, Mangood et al. found that the adsorption of metallic ions increases quickly as the pH of the solution rises within the range of pH 2 to 5 [35].

Fig. 5 shows the interactions of independent variables including pH and reaction time on Cr removal. The impression of time on bio-sorption of Cr was studied at different times ranging from 15 to 75 min. As seen in Fig. 5, by increasing the reaction time and reducing the pH to less than 2, resulted in a significant increase in Cr removal efficiency by the *Prosopis cineraria* adsorbent, reaching over 80%. However, when the pH exceeded 3, the removal rate reached its lowest value and reaction time had no significant impact on it. Sinha et al. [7] showed that Cr removal efficiency using *Prosopis cineraria* adsorbent increased significantly by longer reaction time and lower pH levels of the solution.

3.4. Possible mechanisms of Cr(VI) removal by *Prosopis cineraria*

In order to comprehend the binding of chromium to biomass, it is crucial to pinpoint the functional groups that are responsible for the binding of chromium. When discussing the mechanism of chromium biosorption on biosorbents, it is important to consider various mechanisms such as electrostatic forces, ion-exchange, and chemical complexation. The study confirmed that the removal rate of hexavalent chromium is significantly dependent on pH, decreasing as pH increases. In an acidic environment, hexavalent chromium is likely reduced to trivalent chromium through direct reduction reactions and adsorption of trivalent chromium ions at higher pH values. At very low pH value (pH = 1.1), hexavalent chromium is poorly adsorbed due to electrostatic repulsion [36]. Hexavalent chromium undergoes reduction to trivalent chromium in the water phase through a direct mechanism when it comes into contact with the electron-donor group of biomaterials, which have a lower reduction potential than hexavalent chromium. The trivalent chromium ions then either remain dissolved in water or form complexes with Cr-bonding groups present on the surface of the biosorbent. The absence of detectable Cr (III) content in the filtrate (at pH < 3.0) from the experiments suggests that complexation may play a role in the elimination of hexavalent chromium [37]. The reduction in sorption as pH increases may be attributed to the decrease in electrostatic attraction and the competition between the chromium anionic species ($HCrO_4^-$ and CrO_4^{2-}) and OH^- ions in the solution for adsorption on the active sites of the sorbent [38]. Recent studies confirmed that the highest efficiency in removal was achieved at pH 1.0–2.0. Adsorption coupled with reduction is considered the real mechanism of Cr (VI) removal under acidic conditions. The process of indirect reduction is quite complex and involves three main steps. Initially, the anionic Cr (VI) attaches to positively charged groups on the surface of biomaterials, such as amino groups and carboxyl groups. In

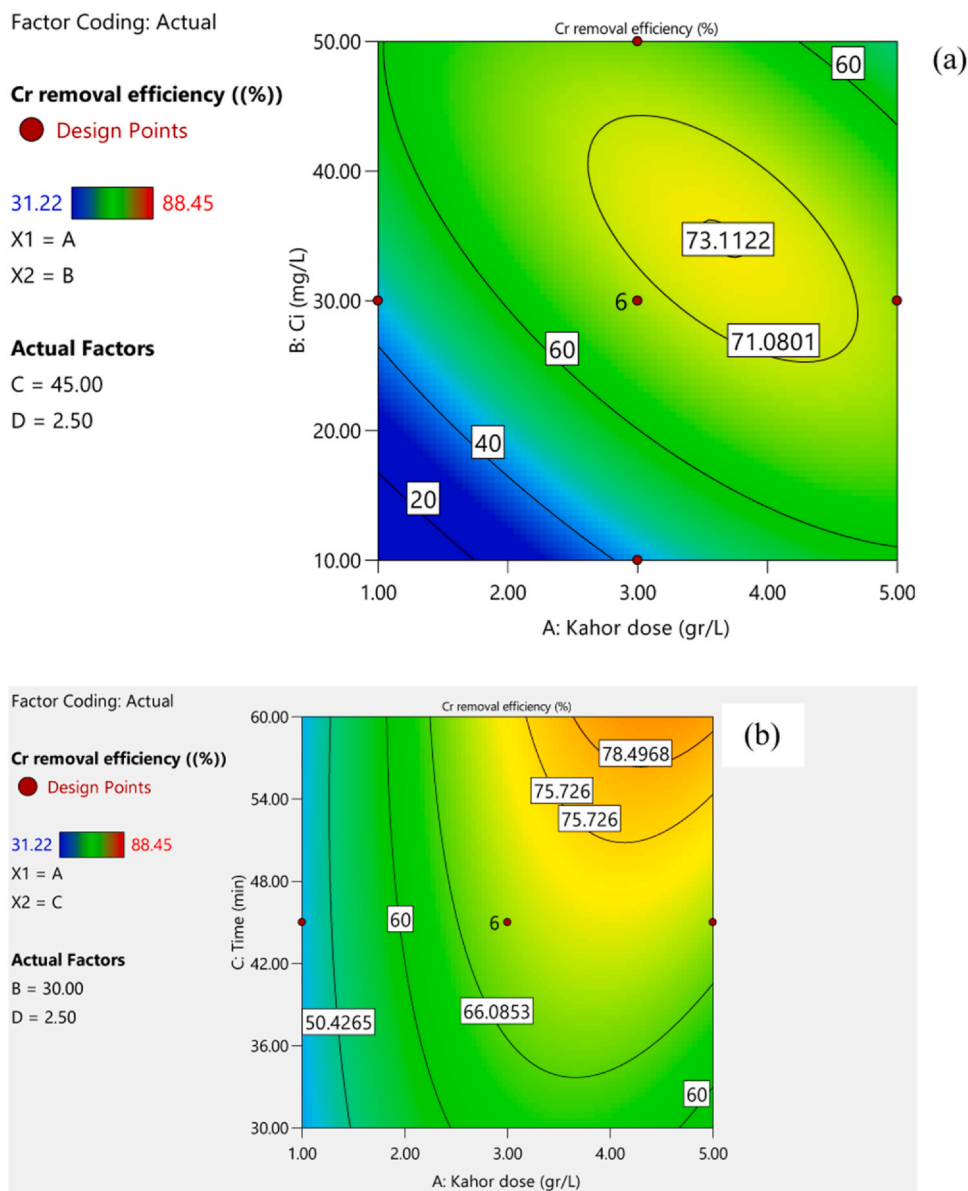


Fig. 3. Two-dimensional response surface diagram for Cr removal efficiency from aqueous solution by *Prosopis cineraria*, (a) initial concentration of chromium versus adsorbent dose of *Prosopis cineraria* (b) reaction time versus *Prosopis cineraria* adsorbent dose.

the next step, it is transformed into Cr (III) with the help of neighboring electron-donor groups, leading to the release of Cr (III) into the aqueous phase. This release occurs due to detachment forces between the positively charged Cr (III) and positively charged groups on the surface of the biomaterials, or due to the formation of complexes of Cr (III) with adjacent groups (Fig. 6) [36,39].

3.5. Numerical optimization

After data analysis, optimization, which is one of the main objectives of RSM, was performed to achieve the optimum values of variables for maximum removal efficiency from the model. As shown in Table 4, the desired goal for chromium removal efficiency was selected as a maximum value of 89.65%, and the variables of *Prosopis cineraria* dose, initial chromium concentration, time, and pH were selected to be within range. Based on the results obtained by the model, the optimal operating conditions are as follows: *Prosopis cineraria* dose of 3.98 g/L, initial chromium concentration of 25.41 mg/L, contact time of 59.82 min and pH of 2.02.

3.6. Investigation of chromium biosorption on *Prosopis cineraria* adsorbent

3.6.1. Adsorption kinetic

Estimating the adsorption rate is valuable during the development of batch adsorption systems. Understanding the kinetics of pollutant absorption is essential for selecting appropriate operating conditions for full-scale batch processes [35].

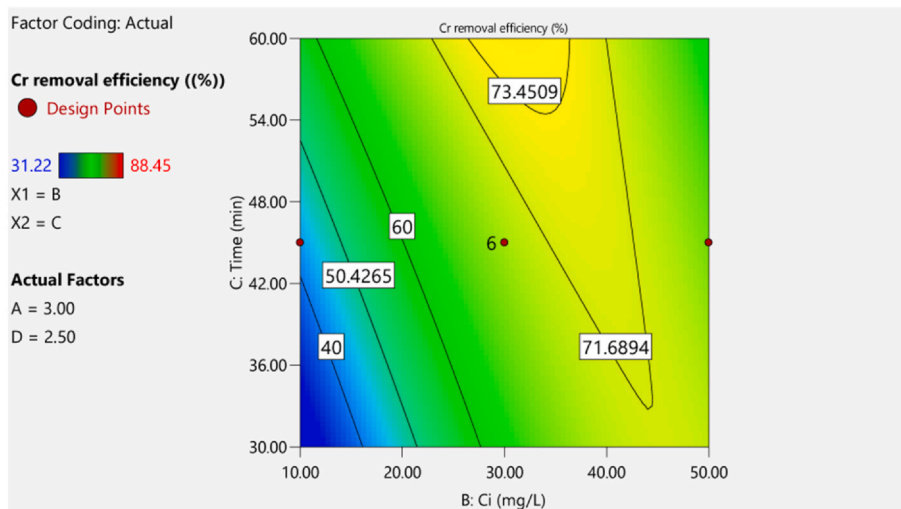
The Pseudo-first-order kinetic model (Eq. (6)) denotes the adsorbent capacity and is used when adsorption happens using the diffusion mechanism from within the boundary layers.

$$\ln(q_{eq} - q) = \ln q_{eq} - \frac{k_1 t}{2.303} \tag{6}$$

where q (mg/g) and q_{eq} are the amount of chromium adsorbed at equilibrium and at time t , k_1 is the rate constant of the first-order rate eq. (1/min). The experimental determination of the adsorption rate constant K_1 involves plotting $\ln(q_e - q_t)$ versus (t) as shown in Fig. 5(A).

The Pseudo-second-order kinetic model (Eq. (7)) is the dominant and controlling mechanism of chemical adsorption in the adsorption

(a)



(b)

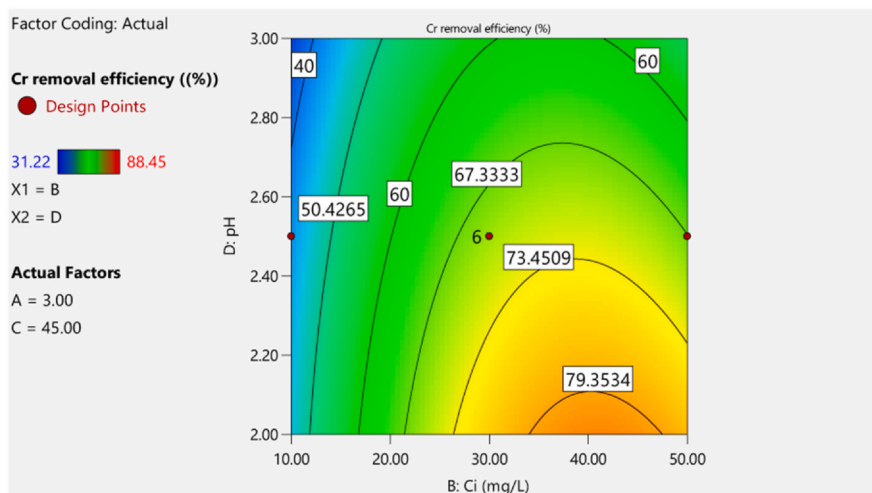


Fig. 4. Two-dimensional response surface diagram for chromium removal efficiency from aqueous solution by *Prosopis cineraria*, (a) initial concentration of chromium versus reaction time (b) initial concentration of chromium versus pH.

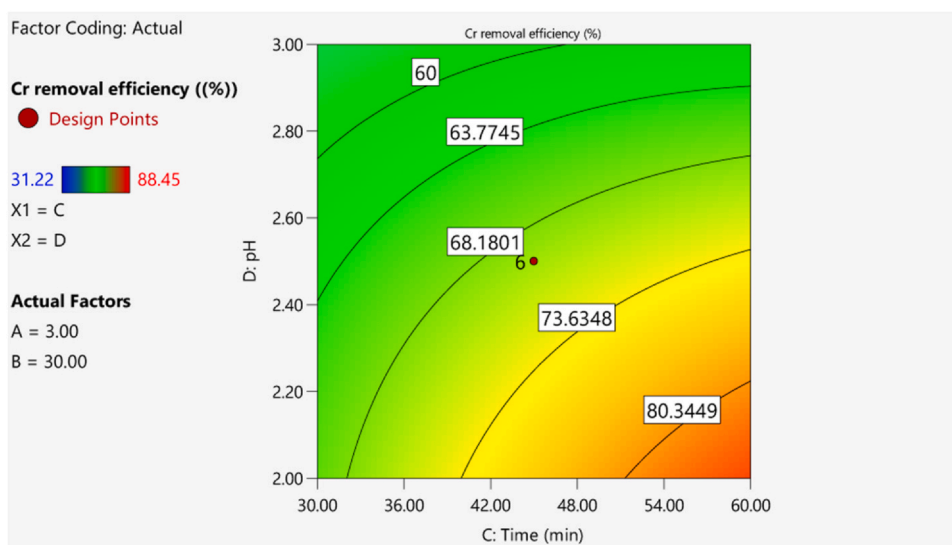


Fig. 5. Two-dimensional response surface diagram for chromium removal efficiency from aqueous solution by *Prosopis cineraria*, pH versus reaction time.

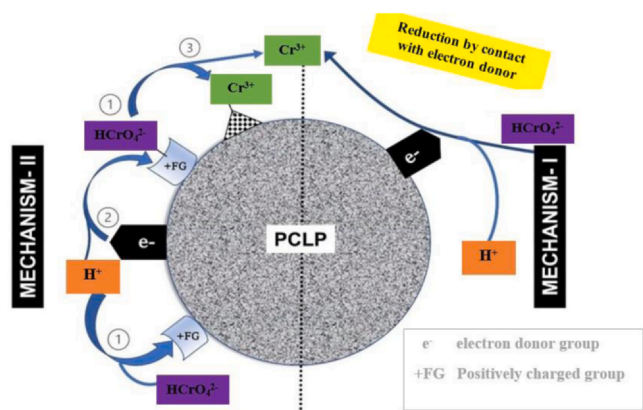


Fig. 6. Possible mechanism of the Cr(VI) biosorption from aqueous system using *Prosopis cineraria* leaf powder (PCLP). Modified after Singh et al. [40].

process and is based on solid-phase adsorption and describes the slowing phase of chemical adsorption [41].

$$\frac{t}{q} = \frac{1}{K_2 q_{eq}^2} + \frac{1}{q_{eq}} t \tag{7}$$

where K_2 is the second-order kinetic constant (g/mg.min) and q_e is the amount adsorbed at equilibrium and at time t . By plotting t/qt versus t , the experimental assessment of the adsorption rate constant K_2 can be determined, and the capacity q_e can be measured from the slope of Fig. 5(B).

Table 5 presents the estimated kinetic data for Cr. The results indicate that the pseudo-first-order kinetic model is suitable for describing Cr removal on *Prosopis cineraria*, as the calculated theoretical q_e , cal values closely match the investigational q_e , exp values, and the coefficient of determination (R^2) values are 0.9613. As a result, it is feasible that the rate-limiting step may involve chemical sorption related to valency forces during electron allocation or interaction between the adsorbent and metal ions. Chemisorption typically only occurs with a single layer of molecules on the surface, but it may be followed by further layers of physically adsorbed molecules. During chemisorption, the adsorbent surface forms a chemical bond, typically covalent, with the heavy metals, causing them to position themselves in a way that increases their coordination with the surface [42].

As shown in Fig. 7A and B, the R^2 value obtained (0.9613) and the proximity of q value (equilibrium absorption) obtained through model (37.8) with q value obtained from laboratory data (36.3) indicated a very high matching of pseudo-first-order kinetic model. In the same vein, Garg et al. [43] also achieved similar results that the adsorption of malachite green dye by *Prosopis cineraria* adsorbent follows the pseudo-first-order kinetic model. However, in contrast to this study, Naemi et al. [44] found that the biosorption of lead by *Chlorella vulgaris* adsorbent follows second-order kinetics. Also, the study of biosorption of copper, cadmium, zinc and lead by *Ulothrix zonata* algae from industrial wastewaters showed that biosorption of heavy metals follows the second-order kinetic equation [45]. In another study, it was observed

Table 4
Numerical Optimization of Chromium Removal by *Prosopis cineraria*.

Optimized Conditions	Efficiency of Chromium Removal (%)		Standard Error	Standard Deviation	Desirability (%)
	Predicted	Actual			
<i>Prosopis cineraria</i> Dose (g/L) = 3.98 Initial concentration of Chromium (mg/L) = 25.41 Time (min) = 59.82 pH = 2.02	88.47	89.65	1.18	± 1.05	100

that the second-order kinetic model ($R^2 = 0.9992$) is more desirable in adsorption of lead ion from aqueous solution by *Prosopis juliflora* adsorbent than the first-order model [46].

3.6.2. Adsorption isotherm

Two commonly used bio-sorption isotherm models, the Langmuir and Freundlich models, were employed to examine the connection between adsorption capacity and equilibrium concentration. These models are crucial for optimizing the utilization of adsorbates as they elucidate the interaction between adsorbates and adsorbents [47].

In the Langmuir isotherm model (Eq. (8)), the layered and homogeneous adsorptive material with the same energy on all adsorbent surfaces explains that no transfer of adsorptive material occurs at the adsorbent surface. On the other hand, it shows the adsorptive material on the adsorbent in the Freundlich model (Eq. (9)) based on multilayer and heterogeneous adsorption [41].

$$\frac{1}{q_e} = \frac{1}{q_m \times b C_e} + \frac{1}{q_m} \tag{8}$$

where C_e is the concentration of chromium in the equilibrium state, q_e is the amount of chromium adsorbed at equilibrium state (mg/L), q_m is the maximum adsorption capacity (mg/g) and b is the constant in Langmuir equation (L/mg).

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{9}$$

where C_e is the concentration of chromium at equilibrium state, q_e is the amount of chromium adsorbed at equilibrium state (mg/L), and k_f (mg/g), and n are the equilibrium constants and depend on the adsorption intensity and capacity.

According to Table 6 and Fig. 8, the results showed that there were high correlation coefficients for the isotherms. However, the Langmuir isotherm model ($R^2 = 0.983$) provided a satisfactory match with the adsorption data of Cr on *Prosopis cineraria* adsorbent. This suggests that the sorption of Cr onto *Prosopis cineraria* took place at specific sites on the surface of the adsorbent, known as monolayer. Therefore, it can be concluded that the chromium adsorption process data by *Prosopis cineraria* follows the Langmuir model. Gupta and Rastogi showed that chromium adsorption with green alga *Oedogonium hatei* followed Langmuir model [48]. Moreover, in the study of Akhtar et al. [49], it was observed that the adsorption characteristics of green alga *Chlorella sorokiniana* for removal of chromium ions showed more adaptation of biosorption behavior with Langmuir model. The results of this study were not consistent with recent literature. For example, investigation of nickel adsorption isotherm by oak fruit ash from aqueous solution showed that laboratory data were better matched with Freundlich isotherm ($R^2 = 0.93$) [50]. Maleki et al. [51] found that both Langmuir and Freundlich models described the absorption of cadmium and copper by modified wheat bran. Sayadi et al. showed that Langmuir model for adsorption of chromium, copper and zinc ions by *Spirogyra* algae had the highest correlation coefficients of 0.9983, 0.9924 and 0.9977, respectively [52].

Table 5
Calculated constants of pseudo-first-order and pseudo-second-order kinetic models of chromium biosorption on *Prosopis cineraria* adsorbent.

C ₀ (mg/L)	q _e , exp (mg/g)	Pseudo-first order model			Pseudo-second order model		
		q ₁ , cal (mg/g)	k ₁ (1/min)	R ₁ ²	q ₂ , cal (mg/g)	k ₂ (g/mg.min)	R ₂ ²
25	36.3	37.8	0.027	0.9613	30.4	0.003	0.9279

C₀: Initial concentration. q_e: The amount of metal absorbed in equilibrium mode. q₁: The amount of adsorption metal first and for first degree. q₂: The amount of adsorption metal grade II. K₁: Constant first-rate reaction speed. K₂: Constant second-rate reaction speed. R₂: Correlation coefficient

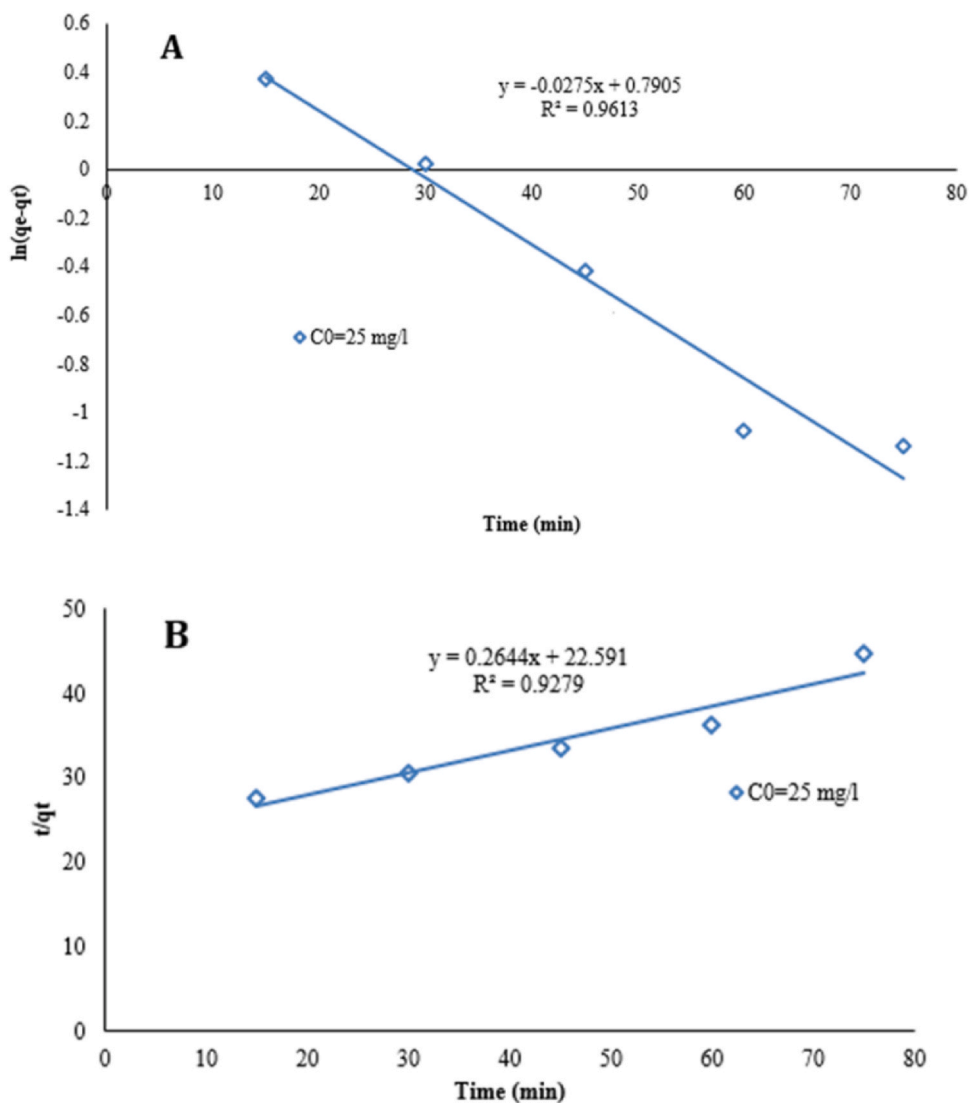


Fig. 7. The pseudo-first-order (A) and pseudo-second-order (B) rate kinetics for the adsorption of chromium on *Prosopis cineraria* adsorbent.

Table 6
Calculated Constants of Langmuir and Freundlich isotherm data of chromium biosorption on *Prosopis cineraria* adsorbent.

Chromium	q _{max}	Langmuir isotherm			Freundlich isotherm		
		K _L	R _L	R ²	K _F	n	R ²
	55.556	0.080	0.046	0.983	8.758	2.907	0.916

q_{max}: Adsorption capacity of single-layer adsorbent. K_L: Langmuir adsorption constant. R_L: Separation coefficient. K_F: Freundlich adsorption constant. n: Surface heterogeneity coefficient. R²: Correlation coefficient

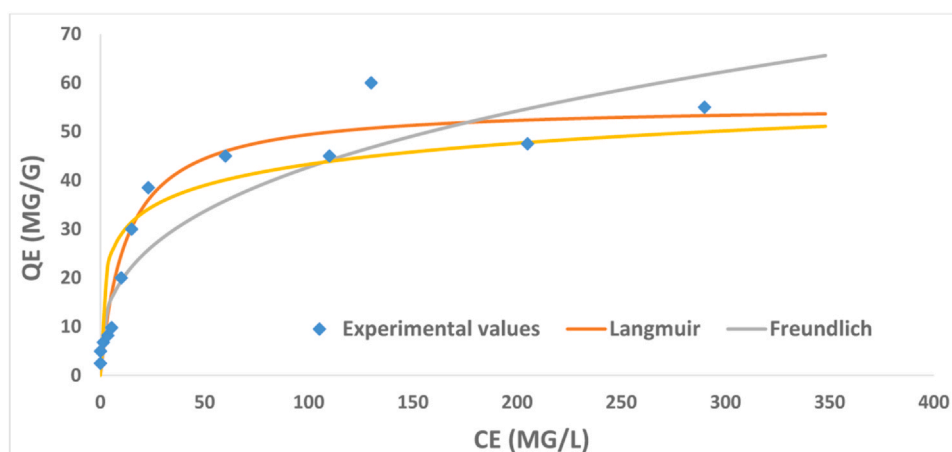


Fig. 8. Langmuir (A) and Freundlich (B) isotherm for chromium biosorption on *Prosopis cineraria* adsorbent.

Table 7

Comparison of adsorption capacities of various biosorbents in chromium removal.

References	Optimized conditions	Adsorption capacity (mg/g)	Adsorbent
[36]	pH = 1.1, adsorbent dosage = 20 g/L	45.1	<i>Fomitopsis pinicola</i>
[53]	pH 5, contact time = 75 min, temperature = 30 °C and biomass dose = 5 g/L	38.4	Rice husk
[54]	pH = 2	76.92	<i>Arundo donax</i>
[55]	pH = 2, time = 120 min	64.82	walnut shell
[56]	pH = 2, initial Cr concentration = 100 mg/L, adsorbent dosage = 2 g/L	14.54	<i>Bacillus subtilis</i>
[57]	pH = 2, initial Cr concentration = 10 mg/L, adsorbent dosage = 1 g/L	18.5	<i>Opuntia cladodes</i>
[58]	pH = 2, initial Cr concentration = 5 mg/L, adsorbent dosage = 2.5 g/L, time = 24 h	15.6	Tella
[59]	pH = 2, initial Cr concentration = 50 mg/L, adsorbent dosage = 10 g/L, time = 1 h	15.17	<i>Rosa canina</i>
Present study	pH = 2.02, initial Cr concentration = 25.41 mg/L, adsorbent dosage = 3.98 g/L, time = 59.82 min	55.55	<i>Prosopis cineraria</i>

3.7. Comparison of *Prosopis cineraria* adsorbent performance with literature

The results reveal that *Prosopis cineraria* achieved maximum removal efficiency of 88.45% at an initial concentration of 20 mg/L, pH of 2, adsorbent concentration of 4 g/L and time of 60 min. Table 7 presents the adsorption capacities of *Prosopis cineraria* compared to those of other biosorbents reported in previous studies. It is evident that the maximum adsorption capacity (Q_{max}) of *Prosopis cineraria* was 55.55 mg/g, which was the highest adsorption compared to most bioadsorbents. The presence of functional groups, high pore volume, and specific surface area enhances the adsorption ability of the biosorbents. Furthermore, the comparison indicates that the biosorbent performed well for chromium removal, providing higher adsorption capacities compared to recent adsorbents such as Rice husk, *Arundo donax*, *Fomitopsis pinicola* and *Bacillus subtilis*. The simplicity and low production expenses are additional advantages of the biosorbent in this study.

4. Conclusions

The *Prosopis cineraria* leaves has been found to effectively adsorb chromium from aqueous solution. The results from the removal experiments indicated that the optimum operational conditions for chromium removal of 65.89% within *Prosopis cineraria* dose of 3.98 g/L, initial chromium concentration of 25.41 mg/L, contact time of 59.82 min and pH of 2.02. The adsorption of chromium by the *Prosopis cineraria* aligns well with the Langmuir isotherm model ($R^2 = 0.983$) and pseudo-first-order kinetic model ($R^2 = 0.9613$). Utilizing the Langmuir adsorption isotherm, we determined a maximum monolayer adsorption capacity (q_{max}) of 55.55 for chromium, indicating the efficacy of the *Prosopis cineraria* surface in adsorbing chromium ions. This q_{max} value suggests a significant affinity for chromium adsorption on

the *Prosopis cineraria* surface. The robust q_{max} value obtained serves as a promising indicator of the high capacity of *Prosopis cineraria* to efficiently adsorb and remove chromium ions from the environment. With *Prosopis cineraria* leaves being cost-effective and easily accessible, this research suggests a practical method for removing chromium from contaminated water or effluents, offering a potential solution for eliminating toxic metals from wastewater. One of the limitations of this study was the use of aqueous solution instead of industrial wastewater to conduct experiments and also not considering temperature as a main variable in chromium adsorption. Future studies should focus on advancing the technical analysis of the adsorption process using *Prosopis cineraria* leaves by conducting SEM analysis to explore surface morphology, examining surface area and pore distribution, and implementing XRD and FTIR analysis to elucidate functional group interactions. These investigations will enhance the understanding of the adsorption mechanisms and provide valuable insights into the potential applications of *Prosopis cineraria* for chromium removal in aqueous solutions, further contributing to the field of heavy metal remediation research.

CRedit authorship contribution statement

Reza Ghanbari: Writing – original draft, Project administration, Funding acquisition, Data curation. **Milad Mousazadehgavan:** Writing – review & editing, Writing – original draft, Validation, Software, Methodology. **Hamzeh Ali Jamali:** Formal analysis. **Maedeh Soleimani:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships.

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Disclosure of potential conflicts of interest

No potential conflict of interest was reported by the author(s).

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