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Application of modified bentonite for efficient water purification: A case of Cr(VI) adsorption

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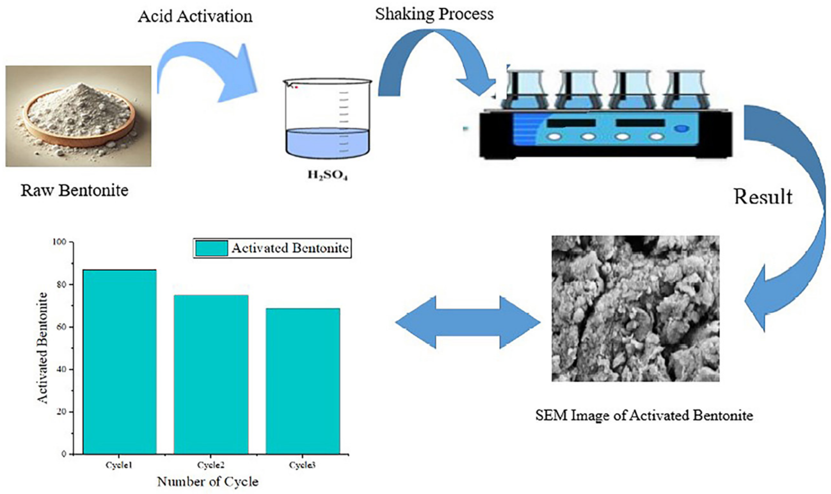
HIGHLIGHTS

- Enhanced adsorption efficiency of acid-activated bentonite for Cr(VI) removal from water.
- 100 % Cr(VI) removal under optimal conditions.
- Fits Langmuir isotherm and pseudo-second order kinetics.
- Spontaneous and exothermic processes, requiring no external energy.
- 92 % Cr(VI) removal from groundwater in Iran's Forumad region.

GRAPHICAL ABSTRACT



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ABSTRACT

This study explores the use of acid-activated bentonite as an efficient adsorbent for removing hexavalent chromium (Cr(VI)) from water. Acid activation enhances the surface area and adsorption capacity of bentonite, improving its water treatment efficiency. Various techniques, including BET, FT-IR, XRD, XRF, and SEM, were used to analyze structural and compositional changes after activation. Adsorption experiments showed that under optimal conditions - room temperature, 0.1 ppm Cr(VI), and 1 g of acid-activated bentonite - 100 % removal was achieved. The adsorption followed the Langmuir isotherm with a maximum capacity of 0.122 $mg.g^{-1}$. Kinetic studies confirmed a pseudo-second-order reaction model ($R^2 = 0.99$), indicating a chemisorption mechanism. Thermodynamic analysis showed the process is spontaneous and exothermic, requiring no external energy input. Groundwater tests from the Forumad region (Semnan Province) compared raw and acid-modified bentonite, revealing a 92 % Cr(VI) removal efficiency with the modified form, reducing contamination to safe levels. These results highlight acid-activated bentonite as a cost-effective, eco-friendly adsorbent for water purification, demonstrating its real-world potential for ensuring safer drinking water.

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1. Introduction

In recent years, contamination of water resources with heavy metals has become a major environmental concern due to these pollutants' toxic, non-biodegradable, and bioaccumulative nature [1,2]. Among them, hexavalent chromium (Cr(VI)) is particularly hazardous and is classified as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC). Cr(VI) can cause severe health problems, including kidney damage, gastrointestinal disorders, and cancer. It primarily enters aquatic systems through industrial effluents from electroplating, leather tanning, dye manufacturing, and stainless steel production. Therefore, effectively removing Cr(VI) from water is essential to ensure environmental and human health. Heavy metals are a group of metallic elements with high atomic weight and density that can be toxic even at low concentrations. Common examples include chromium (Cr), lead (Pb), cadmium (Cd), mercury (Hg), and nickel (Ni). These metals enter water bodies through industrial activities such as mining, electroplating, chemical manufacturing, and municipal wastewater discharge. Due to their non-biodegradability and tendency to bioaccumulate, heavy metals pose serious threats to human health and aquatic ecosystems [3,4]. Among these, hexavalent chromium (Cr(VI)) is one of the most hazardous and persistent contaminants in water.

While effective, conventional Cr(VI) removal techniques, such as ion exchange, membrane filtration, and chemical precipitation, suffer from drawbacks such as high operational costs, energy requirements, and secondary waste generation [5]. In contrast, adsorption has emerged as an efficient and eco-friendly method for water treatment due to its simplicity, cost-effectiveness, and wide availability of adsorbents. Bentonite, a natural clay mineral, is widely studied for adsorption applications owing to its high surface area, cation exchange capacity, and low cost [6,7]. However, raw bentonite is less effective in removing anionic contaminants like Cr(VI), necessitating chemical modification to improve performance.

Acid activation using agents such as sulfuric acid is a common method to enhance the physicochemical properties of bentonite, including its surface area, pore volume, and number of active sites [8,9]. Sulfuric acid, in particular, has proven to be more effective than hydrochloric acid in increasing the adsorption capacity for Cr(VI) [10]. Several studies have reported improved adsorption of heavy metals by acid-activated bentonite. For instance, Moradi *et al.* demonstrated the enhanced performance of sulfuric acid-treated bentonite in removing Cr(VI) from aqueous solutions [9]. Similarly, Ali and Morshed highlighted the efficiency of modified bentonite in adsorbing heavy metals under optimized conditions [11]. Despite promising results, many prior studies have been limited to controlled laboratory conditions and synthetic wastewater. Therefore, there is a need to evaluate adsorbent performance in real environmental settings and to further optimize the operational parameters using robust statistical methods.

In this study, bentonite was modified via sulfuric acid activation and applied to remove Cr(VI) from both synthetic solutions and real groundwater samples collected from the Forumad region in Semnan Province, Iran. Advanced characterization techniques such as XRD, SEM, FT-IR, BET, and XRF were employed to investigate structural and compositional changes in the adsorbent. Response surface methodology (RSM) and Box-Behnken design (BBD) were also used to model and optimize the adsorption process. Kinetic and thermodynamic studies were performed to understand the mechanism and feasibility of the adsorption. This work differs from previous studies by combining material characterization, statistical optimization, and real-sample testing to demonstrate the practical applicability of acid-activated bentonite for Cr(VI) removal.

2. Experimental

2.1. Materials

Raw bentonite was procured from the Niakan Company in Semnan, Iran. The chromium testing tablets were sourced from Wagtech, UK, while potassium dichromate ($K_2Cr_2O_7$) powder and sulfuric acid (H_2SO_4, 98%) were acquired from Merck, Germany, and subsequently utilized in the experimental procedures.

2.2. Chromium (VI) standard solution preparation

To prepare a 1000 ppm standard hexavalent chromium solution, 0.1 g of potassium dichromate ($K_2Cr_2O_7$) powder was dissolved in a 100 ml beaker containing purified water. From this solution, dilute 10 $mg.L^{-1}$ to a final volume of 100 ml to attain the target concentration of 100 ppm. Then, standard solutions with chromium concentration values of 0.1, 0.5, and 1 $mg.L^{-1}$ are prepared using distilled water. The initial concentration of each standard is determined using a spectrophotometer at a wavelength of 540 nm [13,14].

2.3. Raw bentonite adsorbent preparation method

Initially, 100 g of raw bentonite is mixed with distilled water (double-distilled) and allowed to soak for 6 h. After soaking, the wet bentonite is passed through filter paper to partially dry, and then placed in an oven at 120 °C and heated for 6 h to ensure complete drying. Once dry, the bentonite is ground and sieved for uniform particle size [14,15].

2.4. Acid activation procedure for bentonite adsorbent

To activate the bentonite, mix 50 g of raw bentonite with 500 ml of 3 M sulfuric acid solution in a 1000 ml beaker. Heat the mixture to 110 °C under continuous stirring (220 rpm) for 4 h. Quickly stop the reaction by adding 500 ml of ice-cold water and discontinue heating. Filter the suspension and wash the residue with distilled water to remove residual acid. Finally, the acid-treated bentonite is dried at 120 °C for 6 h, then ground and sieved to ensure uniform particle size, ready for adsorption [13].

2.5. Removal of hexavalent chromium

To assess the removal of hexavalent chromium, a specific amount of raw and acid-activated bentonite is mixed with a chromium(VI) solution in a jar test apparatus at 300 rpm (as shown in Fig. 1). After a designated contact time, the solution is separated from the adsorbent using centrifugation, yielding a clear supernatant. Finally, the hexavalent chromium concentration in the supernatant is measured using a spectrophotometer at a wavelength of 540 nm.

The laboratory equipment used in this study includes a WTW Inolab7110 pH meter, a Wagtech 7100 spectrophotometer, a Sartorius laboratory balance with an accuracy of five decimal places, a JTR90 six-position jar test apparatus, a DEMERD oven, and a DHS 700 hot plate magnet.

2.6. Removal of hexavalent chromium in batch mode

Batch adsorption studies were performed in 100 mL conical flasks, mixed using a shaker at a constant speed. Optimal conditions for factors like adsorbent dosage, temperature, and initial chromium(VI) concentration were analyzed using Design Expert software. After the experiments, suspensions were centrifuged, and the final chromium(VI) concentration was measured using a spectrophotometer [16,17].

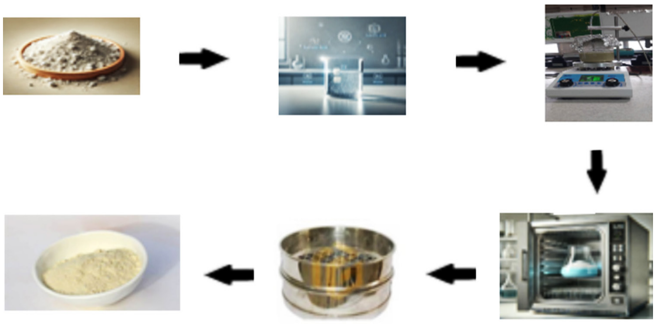

Fig. 1. Process of modifying natural bentonite with sulfuric acid.

The percentage of chromium(VI) removed can be determined using the Eq. (1).

$$R\% = (C_0 - C_f) \times 100/C_0 \tag{1}$$

To calculate the adsorption capacity (q) of the adsorbent, the Eq. (2) can be used.

$$q_e = (C_0 - C_f) \times V/m \tag{2}$$

where, C_0 and C_f represent the starting and ending concentrations of the hexavalent chromium solution, respectively, while V denotes the volume of the solution, and m represents the mass of the adsorbent.

2.7. Investigation of the point of zero charge (pH_{pzc}) in raw bentonite

The point of zero charge pH_{pzc} for raw bentonite was assessed by mixing 0.55 g of bentonite with a hexavalent chromium solution, with the initial pH adjusted between 2 and 10 using nitric acid and sodium hydroxide. The mixture was diluted to reach a total volume of 100 ml.g^{-1}. Subsequently, 0.55 ml of the adjusted solution was placed in a jar test apparatus and blended at 300 rpm over 24 h. The final pH, referred to as pH_f , was measured after the mixing period. By plotting pH_f against the initial pH values, the pH_{pzc} was derived from the intersection of the plotted curve [18,19]. As shown in Fig. 2, the pH at which the bentonite surface has a net zero charge (pH_{pzc}) was determined to be approximately pH = 8.1.

3. Results and discussion

The XRD patterns of raw bentonite (Figs. 3(a) and 3(b)) reveal distinct peaks for montmorillonite (M) at 6°, 19.8°, 34.9°, and 60.3°, confirming its layered structure,

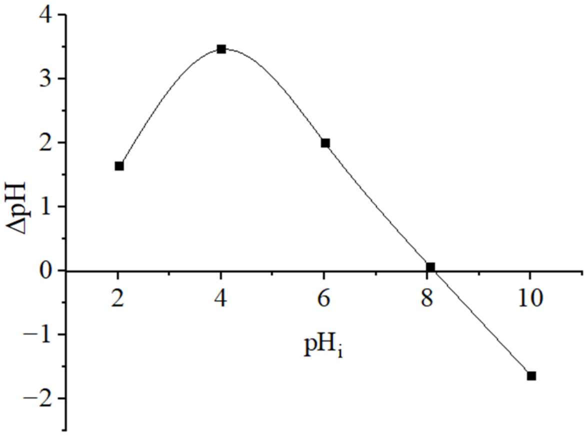

Fig. 2. Changes in the solution pH after 24 h of contact with raw bentonite as a function of the initial pH.

characterized by high cation exchange capacity and significant water absorption. Peaks for clinoptilolite (C) appear at 9°, 11.2°, and 22.3°, along with heulandite (H) peaks at 9° and 23.3°, both exhibiting notable adsorption and ion exchange properties. Quartz (Q) peaks at 26.6° and 50.1° indicate its presence as a stable impurity. In acid-activated bentonite, montmorillonite peaks (5.5°, 19.8°, 34.9°, and 60.3°) persist, demonstrating structural resilience to acid treatment, while the peaks for clinoptilolite and heulandite decrease, suggesting potential structural degradation. Quartz peaks remain unchanged, indicating their stability. Both bentonites exhibit similar crystallinity with varying peak intensities, and new peaks appear in the acid-activated sample, with an expansion in interlayer spacing from 14.72 to 16.04 Å post-acid treatment, indicating structural alterations potentially due to acid infiltration or enhanced water absorption.

The layered structure of raw bentonite (Figs. 4(a) and 4(b)) indicates its natural and intact state, characterized by well-ordered, fibrous layers that provide exceptional properties, including high cation exchange capacity and superior water absorption. In contrast, the irregular and fragmented morphology of acid-activated bentonite reveals that the acid treatment has caused degradation and disintegration of the clay layers, resulting in increased specific surface area and porosity, significantly enhancing its adsorption capacity for contaminants and metal ions.

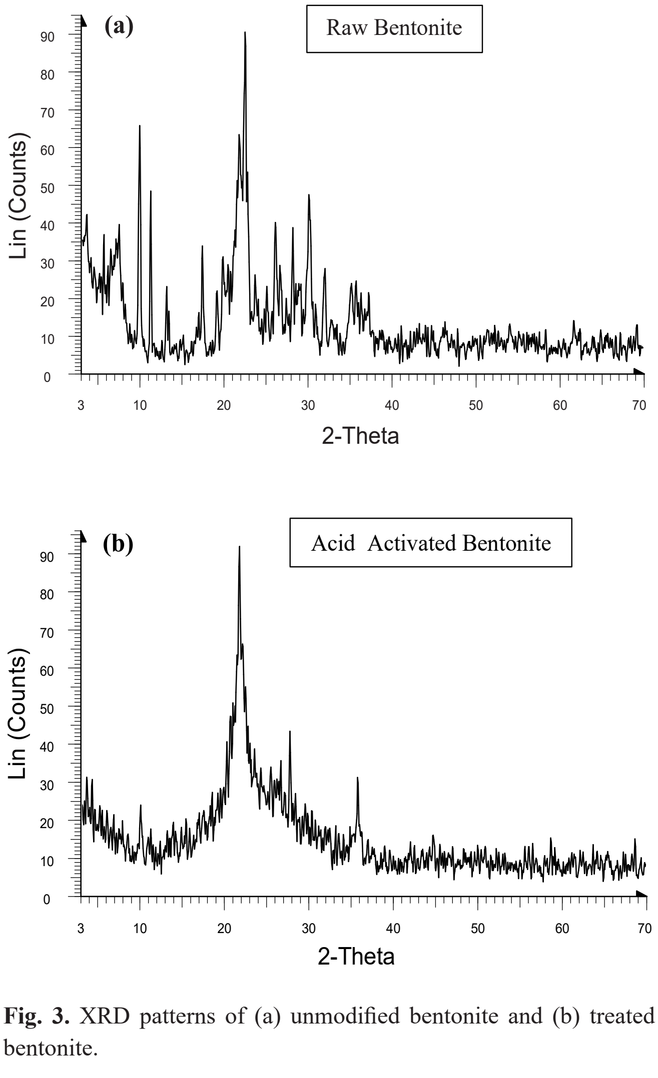

Fig. 3. XRD patterns of (a) unmodified bentonite and (b) treated bentonite.

The FT-IR spectrum analysis of both raw and acid-activated bentonite (Figs. 5(a) and 5(b)) reveals their intricate mineral structures and provides crucial insights into their chemical compositions and functional groups. Key peaks at 3487.06, 3452.34, and 3433.06 cm^{-1} indicate the presence of molecular water and hydroxyl (OH) groups that enhance adsorption capacity, while the peak at 3627.85 cm^{-1} reflects free OH groups. The peak at 1635.52 cm^{-1} shows vibrations of adsorbed water, and the peaks at 1047.27 and 1068.49 cm^{-1} are associated with Si–O–Si stretching vibrations that contribute to structural integrity. The peak at 792.69 cm^{-1} indicates bending modes of Si–O–Si or Si–O–Al, and the peaks at 1609.46, 520.74, and 468.67 cm^{-1} relate to deformational vibrations of Si–O and Al–O bonds,

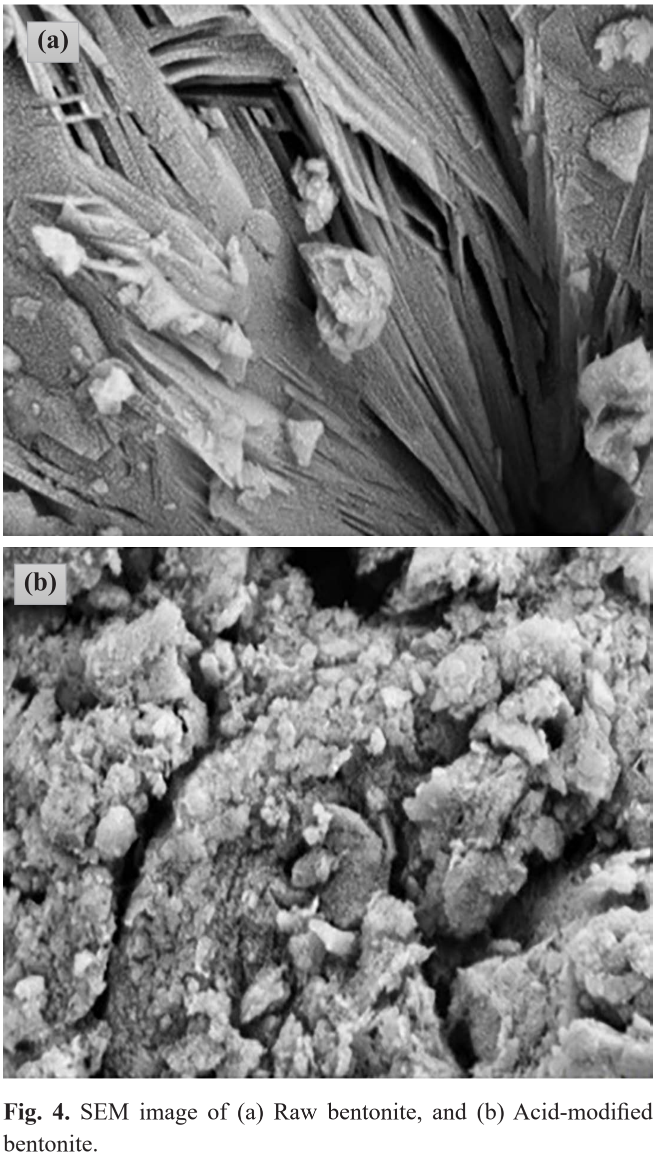

Fig. 4. SEM image of (a) Raw bentonite, and (b) Acid-modified bentonite.

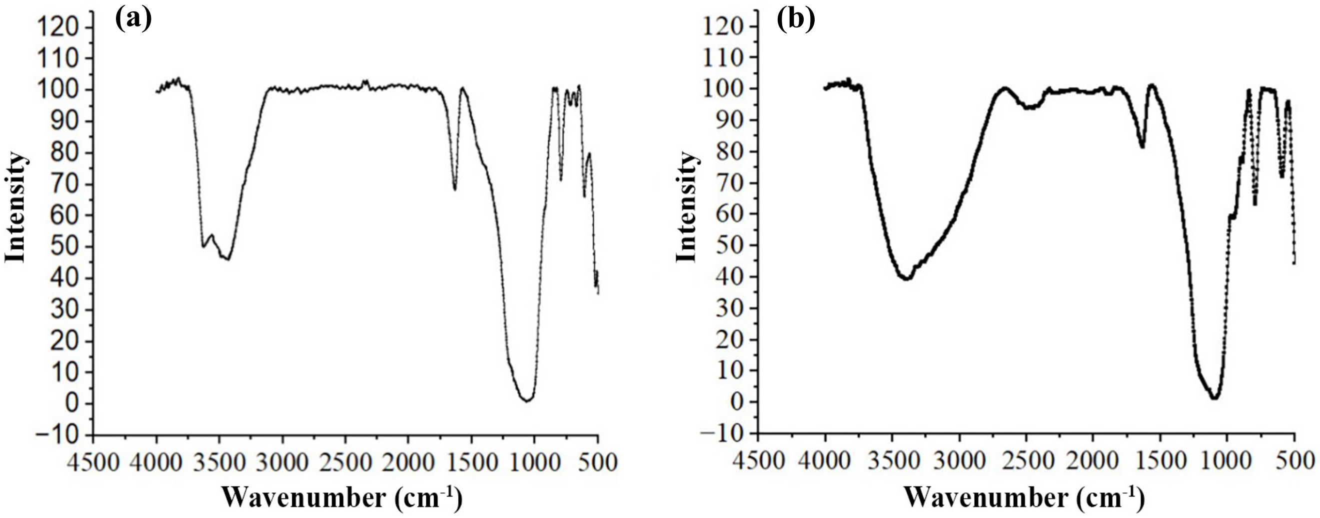

Fig. 5. FT-IR spectra of (a) Raw bentonite, and (b) Acid-modified bentonite.

essential for cation exchange capacity. These observations highlight the significant roles of hydroxyl groups, silicate and aluminosilicate structures, and the presence of water in enhancing the adsorption properties of both types of bentonite.

The textural properties of raw and acid-activated bentonite, as shown by the N_2 adsorption/desorption isotherms in Figs. 6(a) and 6(b), indicate that both samples follow type IV isotherms with H3 hysteresis loops, which are characteristic of layered clays with slit-like mesopores. As shown in Table 1, acid activation significantly increased the specific surface area from 18.33 to 53.42 $m^2.g^{-1}$, while the total pore volume increased from 0.056 to 0.069 $cm^3.g^{-1}$, likely due to particle breakdown and the edge-oapening of clay sheets [20].

3.1. Interaction of parameters and optimization using RSM-BBD

Response surface methodology (RSM) was employed to develop a mathematical model relating independent variables to chromium removal efficiency [21]. The analysis considered temperature (20 - 40 °C) and acid adsorbent concentration (0.1 - 1 $g.L^{-1}$). Table 2 represents the three-dimensional response surface plot, with results summarized in Table 3, detailing removal efficiency and adsorption capacity. Table 4 presents the ANOVA results for the second-order response surface model, showing a total sum of squares of 9290.29, a mean square of 1327.18, an *F*-value of 73.95, and a *p*-value of < 0.0001, confirming the model's significance. The Lack of Fit test yielded a *p*-value of 0.1472, indicating an insignificant lack of fit and confirming the model's adequacy. Table 5 reports the coefficient of determination ($R^2 = 0.9829$) and adjusted R^2 (0.9696), demonstrating that the model explains 98.29 % of the total variability.

Eq. (3) represents the model provided by the software for the response percentage of hexavalent chromium removal:

$$R\,\% = 76.96 - (15.98 \times A) + (26.85 \times B) - (5.19 \times C) + (7668 \times AB) + (4.85 \times AC) - (8.87 \times B^2) - (11.44 \times C^2) \qquad (3)$$

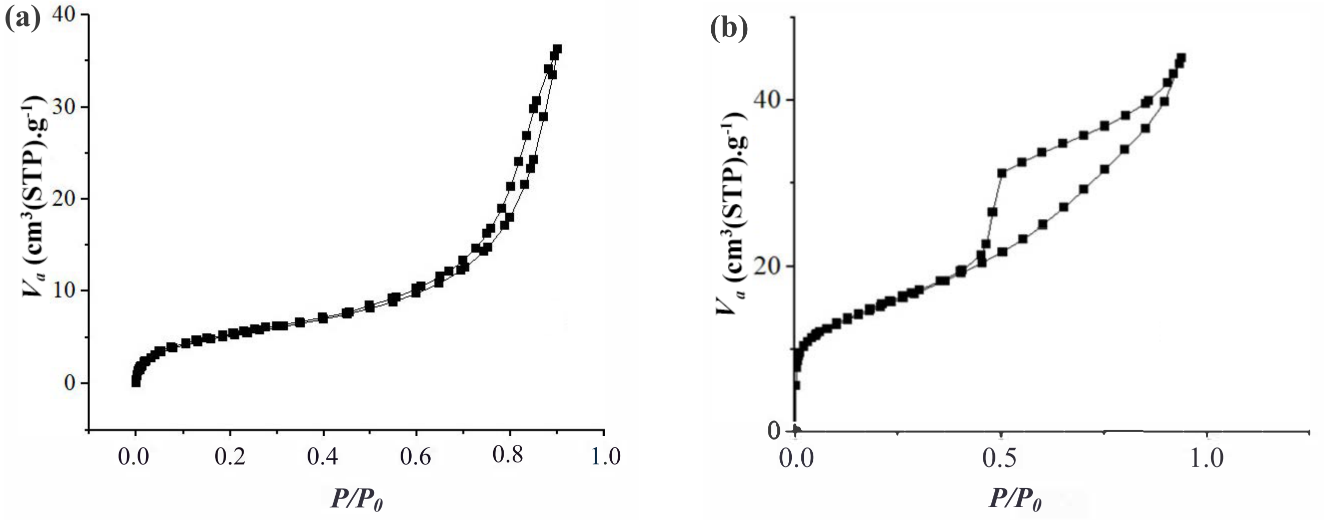

Fig. 6. N_2 Adsorption-desorption isotherm curves of (a) Raw bentonite, and (b) Acid-modified bentonite.

Table 1. Structural pore parameters for natural and acid-activated samples.

Sample	Parameters	Unit	Value
Raw bentonite	V_m	[cm^3(STP).g^{-1}]	4.2125
	as, BET	[m^2.g^{-1}]	18.335
	Total Pore Volume (p/p_0 = 0.901)	[cm^3.g^{-1}]	0.056
	Mean Pore Diameter	[nm]	12.244
Acid-activated bentonite	V_m	[cm^3(STP).g^{-1}]	12.275
	as, BET	[m^2.g^{-1}]	53.426
	Total Pore Volume (p/p_0 = 0.937)	[cm^3.g^{-1}]	0.069
	Mean Pore Diameter	[nm]	5.234

The response surface plot (Fig. 7(a)) indicates that increasing the adsorbent dose improves the removal efficiency of chromium (VI) held at room temperature (30 °C) throughout the process, but excessive dosing may lead to particle aggregation, reducing the effective adsorption surface area. Additionally, the response surface plot (Fig. 7(b)) shows that maximum removal efficiency using acid-activated bentonite occurs at specific temperatures (between 35 to 40 °C) and varying initial chromium concentrations, with higher temperatures enhancing adsorption until potential degradation of the adsorbent occurs.

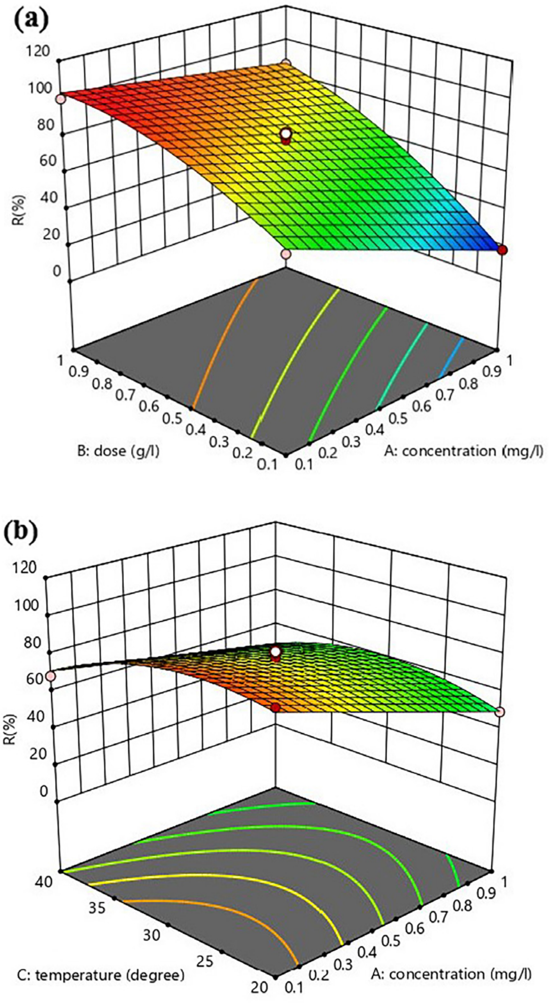

Fig. 7. Response surface plots for Cr(VI) removal, illustrating the interaction effects of (a) adsorbent dose and initial Cr(VI) concentration under an adsorption time of 40 min and ambient temperature, and (b) solution temperature and initial Cr(VI).

Table 2. Design matrix of the experimental factors and their actual values.

A	**Concentration (mg.L^{-1})**	0.5500	0.1000	1.0000
B	**Dose (g)**	0.5500	0.1000	1.0000
C	**Temperature (^{o}C)**	30.00	20.00	40.00

Table 3. BBD experiments for Cr(VI) removal using acid-activated bentonite.

Run	Initial Cr(VI) concentration (mg.L^{-1})	Adsorbent dosage (g)	Temperature (°C)	*R* (%)
1	0.550	0.100	20	30.909
2	0.100	0.100	30	62.500
3	0.550	0.550	30	78.182
4	0.550	1.000	20	90.909
5	0.100	1.000	30	100.000
6	1.000	0.550	40	43.925
7	0.550	0.100	40	30.909
8	0.100	0.550	20	93.750
9	1.000	0.100	30	17.757
10	0.550	0.550	30	76.364
11	0.550	1.000	40	80.000
12	0.550	0.550	30	74.546
13	1.000	0.550	40	68.750
14	0.550	0.550	30	80.000
15	0.550	0.550	30	81.818
16	1.000	0.550	20	49.533
17	1.000	1.000	30	85.981

Table 4. ANOVA results for the second-order response surface model for Cr(VI) removal percentage using acid-activated bentonite.

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value	
Model	9290.29	7	1327.18	73.95	< 0.0001	significant
A - Initial Cr(VI) concentration (mg.L^{-1})	2041.72	1	2041.72	113.76	< 0.0001	
B - Adsorbent dosage (g)	5768.20	1	5768.20	321.39	< 0.0001	
C - Temperature (^{o}C)	215.45	1	215.45	12.00	0.0071	
AB	236.00	1	236.00	13.15	0.0055	
AC	94.02	1	94.02	5.24	0.0479	
B^2	332.04	1	332.04	18.50	0.0020	
C^2	552.39	1	552.39	30.78	0.0004	
Residual	161.53	9	17.95			
Lack of Fit	128.47	5	25.69	3.11	0.1472	not significant
Pure Error	33.06	4	8.26			
Cor Total	9451.82	16				

Table 5. Statistical data for evaluating the reduced model for the response of Cr(VI) removal percentage by acid-activated bentonite.

Standard deviation	4.24	***R²***	0.9829
Mean	67.40	**Adjusted *R²***	0.9696
C.V. %	6.29	**Predicted *R²***	0.9124
		Adeq precision	29.4731

In Fig. 8, Cr(VI) removal efficiency with acid-activated bentonite rises rapidly, reaching 74 % at 20 min and peaking at 89 % at 40 min, indicating abundant active sites. It then slightly decreases to 85 % at 60 min, 82 % at 90 min, and stabilizes around 80 % at 110 min, suggesting adsorption equilibrium. This trend aligns with Moradi *et al.*, where adsorption increased sharply before stabilizing, and the initial rise is due to available active sites, while the decline occurs as Cr(VI) ions at these sites decrease [13].

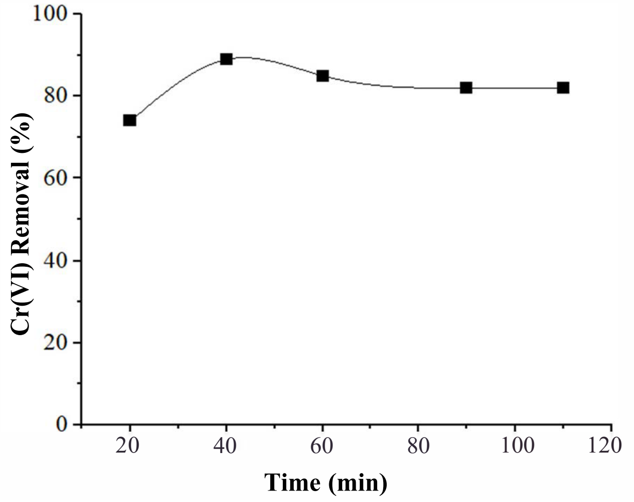

Fig. 8. Time-dependent removal of hexavalent chromium (Cr(VI)) using 0.55 g of both acid-activated and raw adsorbents, with chromium at an initial concentration of 0.55 mg.L^{-1} at temperatures ranging from 25 to 30 ^{o}C.

3.2. Adsorption isotherm

In Figs. 9(a) and 9(b), the adsorption of hexavalent chromium on acid-activated bentonite is best described by the Langmuir model. The Langmuir coefficient of determination is close to 1, indicating a good fit between the data and the model. This suggests that adsorption occurs in a monolayer with uniform energy sites on the surface of the acid-activated bentonite. Table 6 shows that the maximum adsorption capacity (q_m) is 0.122 mg.g^{-1}, and the Langmuir constant (K_l) is 0.047 L.mg^{-1}. The Freundlich model also fits the data to some extent, but it is less accurate as it describes multilayer adsorption on heterogeneous surfaces. In this model, the parameter n is 1.750, and the Freundlich constant (K_f) is 0.047. A similar conclusion was reported by Najafpoor *et al.*, who found that the Langmuir isotherm better described chromium adsorption onto carbon nanotubes compared to the Freundlich model [22].

3.3. Kinetics of adsorption

Fig. 10 shows that the adsorption of hexavalent chromium primarily follows the pseudo-second order kinetic model, which occurs through a chemisorption process driven by

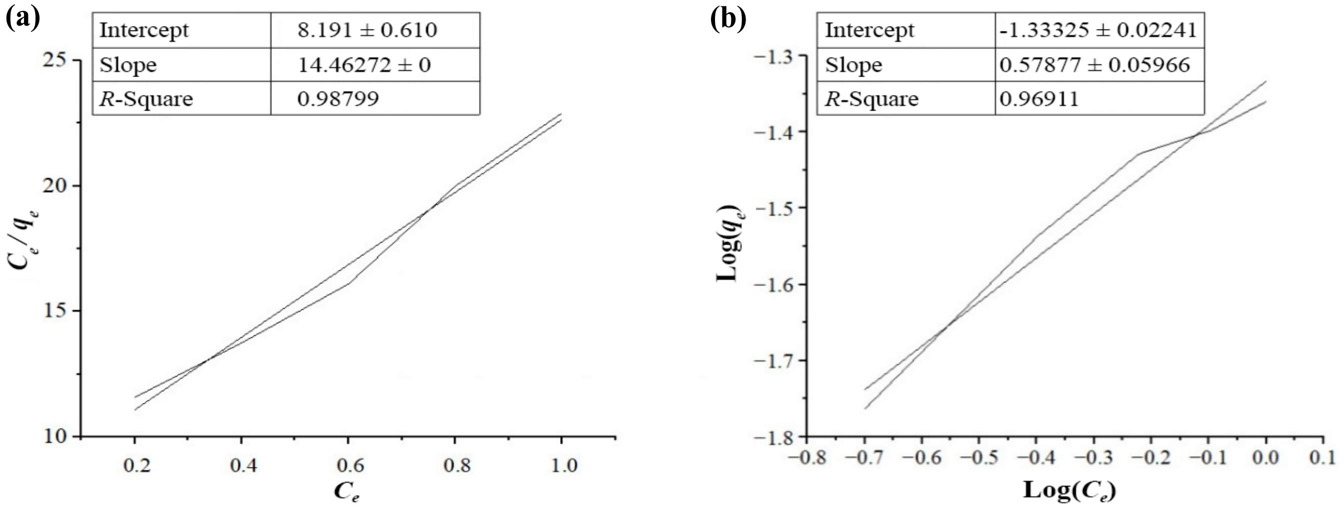

Fig. 9. (a) Langmuir, and (b) Freundlich isotherms, for the adsorption process of Cr(VI) using 0.55 g of acid-activated bentonite at an equilibrium time of 40 min and ambient temperature.

Table 6. The results of the Langmuir and Freundlich isotherms for the removal of Cr(VI) with acid-activated bentonite reveal.

Isotherm Model	Parameter	Value±Error	Coefficient of determination
Langmuir	q_m (mg.g^{-1})	0.122	0.988
	K_l (L.mg^{-1})	0.047	
Freundlich	n	1.750	0.969
	K_f	0.047	

interactions between Cr(VI) ions and the active sites on the adsorbent surface. In a study by Tarmizi Taher *et al.*, the pseudo-second order model demonstrated a more precise linear fit compared to the pseudo-first order model [23]. In this study, the coefficient of determination (R^2) for the pseudo-second order model exceeded 0.982, and the calculated q_e value was nearly identical to the experimental q_e. The results presented in Fig. 9 confirm that the pseudo-second order model more accurately describes the kinetics of Cr(VI) adsorption.

For the pseudo-first-order model, the rate constant (K_1) was 0.0146 min^{-1}, the adsorption capacity (q_e) was 0.0062 mg.g^{-1}, and the coefficient of determination (R^2) was 0.8807. In contrast, for the pseudo-second order model, the rate constant (K_2) was 13.51 min^{-1}, the adsorption capacity (q_e) was 0.041 mg.g^{-1}, and the coefficient of determination (R^2) was 0.9989. These results indicate that the pseudo-second order model provides a significantly better fit to the experimental data, as stated in Table 7.

3.4. Thermodynamic study of the adsorption process

The thermodynamic parameters of Cr(VI) adsorption,

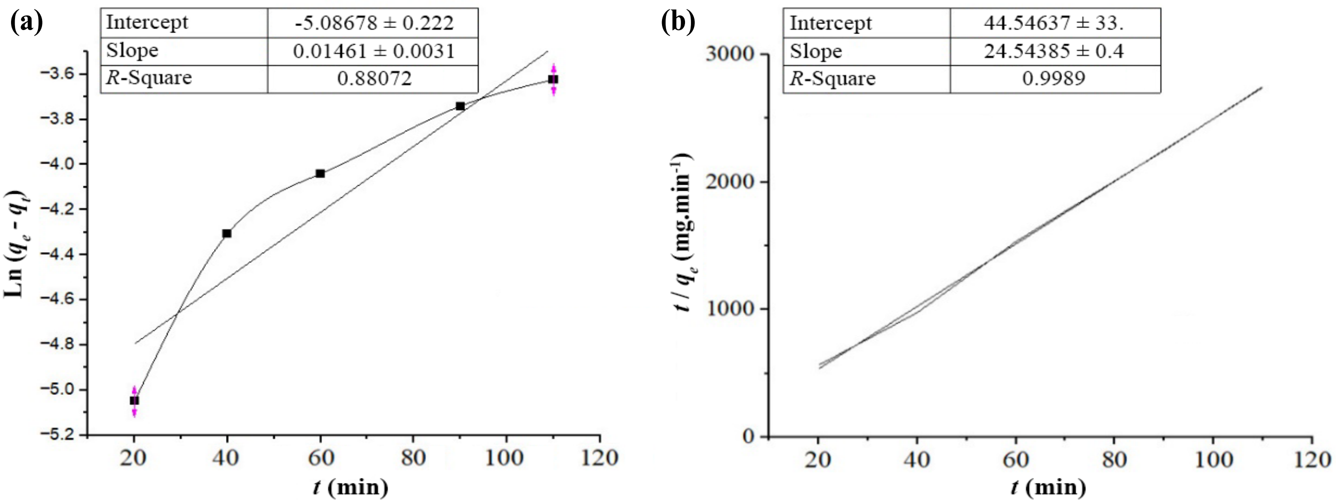

Fig. 10. (a) Pseudo-first order kinetics, and (b) Pseudo-second order kinetics for the adsorption of Cr(VI) onto the modified bentonite.

Table 7. Kinetic parameters of the pseudo-first-order and pseudo-second-order models for the adsorption of Cr(VI).

Adsorption kinetics	**Model parameter**	**Value**
First Order	K_1 (min^{-1})	0.0146
	q_e (mg.g^{-1})	0.0062
	R^2	0.8807
Second Order	K_2 (min^{-1})	13.51
	q_e (mg.g^{-1})	0.041
	R^2	0.9989

including enthalpy ($\Delta H°$), entropy ($\Delta S°$), and Gibbs free energy ($\Delta G°$), were analyzed to assess temperature effects (Eqs. (4)-(7)). Experiments at 20 - 40 °C determined $\Delta H°$ and $\Delta S°$ from the slope and intercept of the lnK_d vs. $1/T$ plot. The adsorption process is exothermic if $\Delta H°$ is negative and endothermic if positive. Key parameters include C_a and C_e (adsorbed and solution-phase concentrations), q_e (equilibrium adsorption capacity), R (gas constant), T (temperature), and K_d (distribution coefficient) [24].

$$K_d = C_a / C_e \tag{4}$$

$$\Delta G = RT \ln K_d \tag{5}$$

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

$$\ln K_d = (\Delta S/R) - (\Delta H/RT) \tag{7}$$

Fig. 11 presents the thermodynamic characteristics of chromium adsorption on acid-activated bentonite at various temperatures. The adsorption process is exothermic, with an enthalpy change (ΔH) of -24.82 kJ.mol^{-1}, indicating strong interactions between the adsorbate and the surface. The negative entropy change (ΔS) of -68.94 J.mol^{-1}.K^{-1} suggests a decrease in molecular disorder, pointing to a more organized adsorption process. Moreover, the negative Gibbs free energy (ΔG) values confirm the spontaneity of the process. Specifically, at 20 °C, ΔG is -4.60 kJ.mol^{-1}; at 30 °C, it is -3.91 kJ.mol^{-1}; and at 40 °C, it is -3.22 kJ.mol^{-1}. The reduction in the magnitude of ΔG with increasing temperature indicates a slight decrease in spontaneity at higher temperatures, as shown in Table 8 [4].

Table 8. Thermodynamic parameters governing Cr(VI) adsorption.

Parameter	**Value**	**Unit**
ΔH	-24.82	kJ.mol^{-1}
ΔS	-68.94	J.mol^{-1}.K^{-1}
ΔG *(Temperature)*	-4.60 (20)	kJ.mol^{-1} (°C)
	-3.91(30)	
	-3.22 (40)	

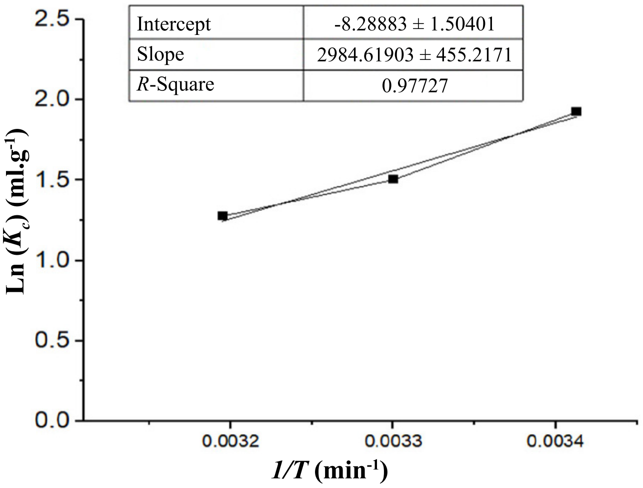

Fig. 11. Thermodynamics of adsorption.

3.5. Comparison of Cr(VI) removal efficiency using acid-activated and raw bentonite in municipal water of Farumad region

Fig. 12 compares the efficiency of raw and acid-activated bentonite from the Farumad region (Semnan Province, Iran) in removing hexavalent chromium from municipal water. Raw bentonite removed only 15.38 % of chromium, due to its limited adsorption capacity. In contrast, acid-activated bentonite achieved a 92.31 % removal rate, showing significantly better performance. The acid activation process enhanced its surface area, active site dispersion,

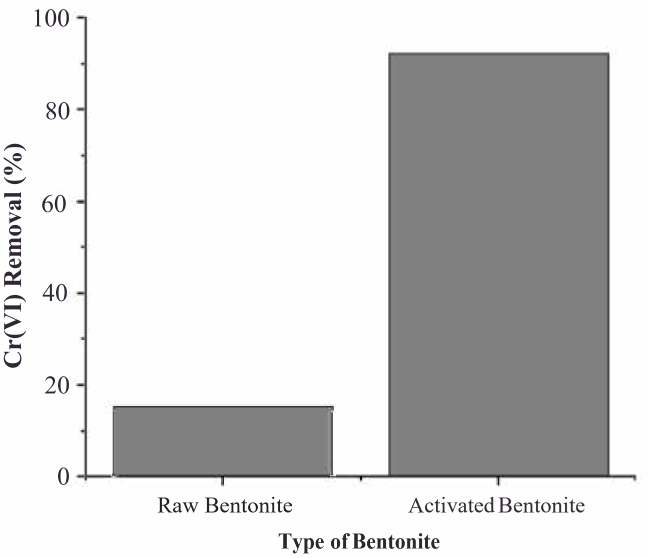

Fig. 12. Comparison of Cr(VI) removal efficiency from municipal water using raw and acid-activated bentonite.

and reactivity, making it a more efficient and cost-effective solution for chromium removal.

3.6. Recovery of acidic bentonite after adsorption of Cr(VI)

Fig. 13 illustrates that acid-activated bentonite exhibited the highest efficiency in Cr(VI) removal during a three-step recovery process, with removal rates of 84 % in the first stage, 71 % in the second, and 64 % in the third. The high removal efficiency in the initial stage reflects the full availability of active adsorption sites. The subsequent decline in efficiency is likely due to the progressive saturation of these sites, indicating a gradual reduction in adsorption capacity and suggesting that the bentonite is nearing the end of its effective adsorption lifespan.

Table 9 shows the maximum adsorption capacity (q_m) of various adsorbents for Cr(VI). As indicated in this study, acid-modified bentonite exhibited a q_m value of 0.122 mg.g^{-1}. In contrast, other adsorbents, such as fly ash (q_m = 0.57 mg.g^{-1}) and corn cob (q_m = 0.28 mg.g^{-1}), demonstrated higher maximum adsorption capacities. Although acid-modified bentonite shows a lower qm value, it may still offer significant advantages in specific applications, particularly in terms of cost-effectiveness, availability, and environmental impact.

4. Conclusion

This study demonstrates that acid-activated bentonite is an effective and cost-efficient adsorbent for removing hexavalent chromium from contaminated water. Increasing the adsorbent dosage improves removal efficiency, while higher Cr(VI) concentrations reduce it. The optimal conditions for maximum removal efficiency are low temperatures and concentrations. The adsorption kinetics follow a pseudo-second order model, indicating chemisorption, with a high R^2 value of 0.9989. The Langmuir isotherm model best describes the adsorption data, suggesting monolayer adsorption on uniform active sites. Thermodynamic analysis shows an exothermic process, with negative enthalpy and Gibbs free energy, confirming spontaneity. Despite lower efficiency compared to other adsorbents, acid-activated bentonite's low cost, reusability, and effectiveness make it a promising alternative for large-scale removal of heavy metals, especially in industrial applications, contributing to environmental protection and safe water access.

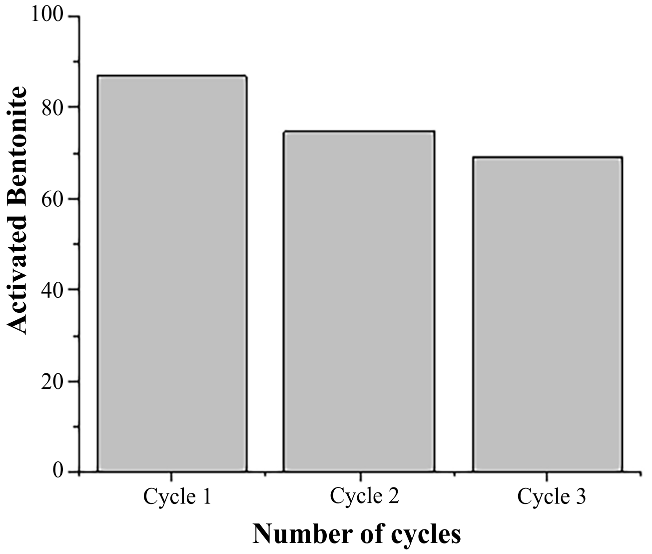

Fig. 13. Three-step recovery process of acid-modified bentonite Cr(VI) removal.

Table 9. Maximum adsorption capacity (q_m) of various Cr(VI) adsorbents.

Adsorbent	q_m (mg.g^{-1})	Reference
Fly ash	0.57	[25]
Corn cob	0.28	[4]
Orange peel powder	4.67	[26]
Pine nut shell	6.06	[27]
Acid-modified bentonite	0.122	This study

Credit authorship contribution statement

Zahra Jelodari: Writing – Original draft, Visualization, Validation, Methodology, Investigation, Formal, and Conceptualization. **Maryam Khajenoori** and **Pouya Mottahedin**: Writing – Review and editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, and Conceptualization.

Conflict of interest declaration

The authors state that they have no financial interests or personal relationships that could have affected the findings of this study.

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Data availability

All data generated or analysed during this study are included in this published article.

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