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Kinetic and Isotherm of Hexavalent Chromium Adsorption onto Nano Hydroxyapatite

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ABSTRACT

Background: Hexavalent chromium (Cr (VI)) is an important contaminant in surface and groundwater and its removal from contaminated water and wastewater has received interest in recent years. This study aimed to explain the removal process of Cr (VI) from aqueous solution using nano hydroxyapatite (n-HAp) as an adsorbent material.

Methods: Cr (VI) removal experiments with the prepared n-HAp were carried out as the batch test in 100 ml flask while agitating on the shaker. The influence of pH (3 to 11), contact time (3-60 min), Cr (VI) concentration (1 to 2 mg/L) and adsorbent dosage (0.025 to 1 g/L) were explored. Three isotherms models and eight kinetics models were used to evaluate the experimental data, respectively. For validation of kinetic and isotherm data, correlation coefficient, sum of square errors (SSE) and normalized deviation were used.

Results: The removal efficiency of Cr (VI) was improved an increase in Cr (VI) and n-HAp concentration. The results best fitted with Langmuir model and the pseudo-second-order rate reaction. Analysis of data with Dubinin-Radushkevich isotherm showed that the adsorption of Cr (VI) onto synthetic n-HAp is a chemisorption process.

Conclusion: The n-HAp as an ecofriendly compound is effective adsorbent for the removal of Cr (VI) from aqueous solution. Accordingly, n-HAp is feasible and promise adsorbent for treating polluted Cr (VI) groundwater.

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Introduction

Since heavy metals are not biodegradable and tend to accumulate in organisms, they are very toxic¹⁻⁵. Chromium is one of the main heavy metals that its anions can be found in water with different oxidation states. The hexavalent chromium (Cr (VI)) is 500 times

more harmful than the trivalent type^{4,6}. This type of chromium has numerous toxic possessions on human health as well as epithelia and skin irritation, lung cancer, kidney, liver and gastric damages, dermatitis asthma, nasal septum and pneumonitis^{4,6,7}. Ever since the confirmation of carcinogenic characteristics of Cr

(VI), the responsible organizations such as the World Health Organization (WHO) and US-Environmental Protect Agency (EPA) improved their standards in drinking water⁶⁻⁸. Based on these standard, the maximum concentration level of Cr (VI) in drinking water should not exceed 0.05 mg/l^{1,6}. As a result of health effects of Cr (VI) and restriction of its permissible concentration for the release on surface water, removing of the surplus level of this contaminant from water and waste streams should be carried out by the suitable techniques⁹.

Several techniques have been investigated for the removal of Cr (VI) from water¹⁰. However, the adsorption processes are the most effective techniques for removal of environmentally hazardous metals, because it is easy to remove the adsorbent from aqueous media after treatment. Further, the sorption technique is generally considered to be a promising method and has been proposed for chromate removal as well¹¹. Different sorbent have been used for the elimination of the Cr (VI) from water and waste streams^{9,11}. A number of adsorbents are expensive and this constraint can be improved with the appropriate assortment and purpose of the low-cost adsorbent materials.

Currently, nanomaterial employed as a promising application in a variety of fields to remove toxic chemicals from water¹². Nanoparticles, due to higher surface area and adsorption ability compared to the traditional materials, are widely used as adsorbent to remove the pollutants from aqueous solutions. In these regards, nanocrystalline hydroxyapatite has been applied as adsorbent to remove heavy metals including cadmium, lead, zinc, cobalt, and oxovanadium. nano hydroxyapatite (n- HAp) is a calcium phosphate based bio ceramic and has been used in medical. n-HAp is manufactured through some of ceramic processing routes including precipitation, sol-gel, hydrothermal processing routes, etc. However, the most attractive technique for the preparation of n-HAp is the precipitation method. This method is very simple, cost effective and ecofriendly that makes the process easy and acceptable by the users¹²⁻¹⁷.

To our knowledge, the adsorption and removal of Cr (VI) via n-HAp has not been considered. Hence, the capability of synthesized n-HAp for removal of the Cr (VI) from aqueous solution has been investigated. The effects of adsorbent dosage, pH, Cr (VI) concentration, and contact time on removal of Cr (VI) were examined. Under optimal experimental conditions, the kinetics and isotherms adsorption of Cr (VI) were also carried out.

Methods

This study was performed for investigation of capability of n-HAp as adsorbent in the removal of Cr (VI) from aqueous solution during 2011 to 2012. All of chemicals and reagents were of analytical grade that were used without further purification (Merck Co., Germany). n-HAp was synthesized and characterized according to the procedure described previously by Sairam Sundaram et al. and Sheha^{12,15}. Briefly, the manufacture of n-HAp involved the initial formation of 0.5 M Ca (OH)₂ suspension. The suspension was then strongly stirred and heated for 1 h before and during the acid addition. Then, appropriate amounts of orthophosphoric acid was added drop wise at a drip rate of 1–2 drops to until form a gelatinous precipitate. The final pH of the solution was controlled by the addition of ammonia solution. During the synthesis process, the Ca:P molar ratio was maintained at 1.67. The precipitate was left in the mother solution overnight and supernatant was decanted. Next, the precipitates were obtained and then were oven dried at 80°C overnight. After that, the dried products were calcined at 400°C to obtain a fine nanocrystalline of Ca₁₀PO₄(OH)₂ powder. Finally, The Ca₁₀PO₄(OH)₂ powder were used as the adsorbent for the removal of Cr (VI).

n-HAp produced was characterized for solid phase, specific surface area, size and pH of point of zero charge (pH_{pzc}). The mean diameter ($D_{Average}$) of n-HAp powders were determined by the Debye-Scherrer equation from the respective XRD patterns (Equation 1):

$$D_A = \frac{K\lambda}{\beta \cos(\theta)} \quad (1)$$

where k is a constant, λ is the x-ray wavelength, β is the line broadening at half the max-

imum intensity in radians, and θ is the Bragg angle, respectively¹⁶.

The specific surface area of n-HAp was determined through Brunauer-Emmett-Teller (BET) methods using a Micrometrics particle size analyzer (model ASAP 2000). The pH of point of zero charge (pH_{pzc}) for n-HAp was determined as Ghanizadeh and asgari study¹⁸.

To assess the ability of n-HAp to adsorb Cr (VI) and determine the most effective values of experimental parameters such as pH, contact time, concentration of Cr (VI), and adsorbent dose in adsorption processes, a series of batch tests was conducted using a shaker-incubator instrument. The stock solution of Cr (VI) was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in 1.0 L of distilled water. The examination solutions were readied by means of following dilution of stock solution to gain the desired concentrations.

Adsorption experimental was made in 100 ml flasks. The flasks and solutions were stirred with a shaker at 100 rpm at room temperature. After completing the mixing operation, the adsorbent was separated by centrifugation (Eppendorf 5810R). The residual Cr (VI) was determined according to standard methods¹⁹.

Equations (2) and (3) were used to calculate the chromium removal efficiency (RE) and equilibrium adsorption capacity.

$$RE(\%) = \left(\frac{C_{\text{ini}} - C_t}{C_{\text{ini}}} \right) \times 100 \quad (2)$$

$$q_e = \frac{V}{M} \times (C_{\text{ini}} - C_t) \quad (3)$$

where, C_{ini} and C_t are initial concentration and the equilibrium of Cr (VI) (mg/L) at time t , respectively; q_e is equilibrium Cr (VI) concentration on adsorbent (mg/g), V is the volume of solution (L) and M is the mass of the used n-HAp sample (g)¹⁸. Apart from the correlation coefficient (R^2), the applicability of the isotherm equations is quantitatively judged by comparing a normalized deviation $\Delta_g(\%)$, which can be described as:

$$\Delta_g(\%) = 100 \times \sqrt{\frac{\sum_{i=1}^N [(q_{e,\text{exp}} - q_{e,\text{cal}}) / q_{e,\text{exp}}]^2}{(n-1)}} \quad (4)$$

where $q_{e,\text{exp}}$ is observed from the batch experiment, $q_{e,\text{cal}}$ is estimated from the isotherm for corresponding $q_{e,\text{exp}}$, and n is the number of measurements in experimental isotherm. The smaller of $\Delta_g(\%)$ value indicates the better isotherm fitting^{20,21,22}. Apart from the correlation coefficient (R^2) in the kinetics studies, the validity of kinetic models for the sorption data have been evaluated by calculating the sum of squared errors (SSE) which can be expressed as:

$$SSE = \sum \frac{(q_{t,\text{exp}} - q_{t,\text{cal}})^2}{q_{t,\text{exp}}^2} \quad (5)$$

Where $q_{t,\text{exp}}$ (mg/g) is experimental sorption capacity of Cr (VI) on n-HAp at time t and $q_{t,\text{cal}}$ (mg/g) was obtained from the kinetic models. The lower values of SSE indicate the better fit of the model^{12,21}.

In this study, the Langmuir isotherms were chosen to determine the maximum adsorption capacity corresponding to the complete monolayer coverage on n-HAp²³. The linear form of the Langmuir isotherms is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bQ_{\text{max}}} + \frac{C_e}{Q_{\text{max}}} \quad (6)$$

In the Langmuir equations, Q_{max} (mg/g) and b are constant and can be determined from the slope and intercept¹⁸.

In this work, Freundlich isotherm was used to estimate the adsorption intensity of the Cr (VI) on n-HAp surface based on sorption heterogeneous energetic distribution of active sites attended by interactions between adsorbed molecules¹. Freundlich model can be expressed by the following equation:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (7)$$

where k_f and $1/n$ are constants that depict the adsorption capacity and the adsorption intensity, respectively. Langmuir and Freundlich isotherms give no information about mechanisms and the energy needed for adsorption. This information can be obtained using the D-R isotherm as mentioned in the following form:

$$\ln q_e = \ln Q_{\max} - K_{DR} \varepsilon^2 \quad (8)$$

In the D-R model, ε (Polanyi potential) is $RT \ln(1+1/C_e)$, Q_{\max} is the adsorption capacity (mg/g), K_{DR} is a constant related to adsorption energy and finally R and T are the gas constant and temperature (K^0), respectively¹. The value of K_{DR} ($\text{mol}^2/(\text{kJ}^2)$) can be calculated from the slope of the plot of $\ln q_e$ versus ε^2 , and Q_{\max} (mg/g) is determined from the intercept.

Results

The results of X-ray diffraction (XRD) spectra (not shown) of the synthesized n-HAp demonstrated that the formation of hydroxyapatite structure, with the highest intensity peaks related to calcium phosphate (hydroxyapatite [HAp]). The mean size of the n-HAp powder that was calculated using Eq. 1 indicated that the size of the synthesized powder is about 53 nm. The nitrogen adsorption-desorption isotherm (data not shown) indicated that the BET surface area of n-HAp powder is $100 \text{ m}^2/\text{g}$. The pH_{pzc} for n-HAp that was determined from draft method was found to be 7.8.

Figure 1 shows the means of three replicates experiments in the terms of Cr (VI) removal and adsorption capacity versus the pH where concentration of Cr (VI), concentration of n-HAp and contact time was fixed at 1.5 mg/L, 0.1 g/L and 60 min, respectively. The results indicate that Cr (VI) adsorption onto n-HAp considerably affected by pH values. As Figure 1 illustrate, when the pH of solution increased from 3 to 7, the average degree of Cr (VI) removal increased from 92 to 98%. Maximum chromium adsorption occurred at pH 7. It is advantageous for the treatment of groundwater where typically has pH 7-8. Therefore, the pH of water does not need to be adjusted for efficient adsorption.

The effect of n-HAp on Cr (VI) adsorption was investigated by varying the n-HAp dose from 0.025 to 1 g/L using 1.5 mg/L chromium solution at pH 7.0. The results of removal of chromium (%) at various n-HAp doses are presented in Figure 2. This figure shows that adsorption increases with increase in n-HAp concentration from 0.025 to 0.1 g/L. Also referring to Figure 2, at 0.1 g/L of n-HAp, residual con-

centration of pollutant reached lower than maximum allowable concentration recommended by WHO.

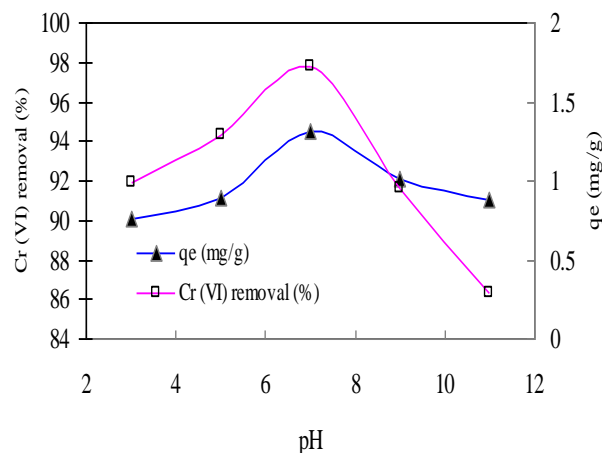


Figure 1: Hexavalent chromium (Cr (VI)) removal efficiency of nano hydroxyapatite (n-HAp) as a function of solution pH

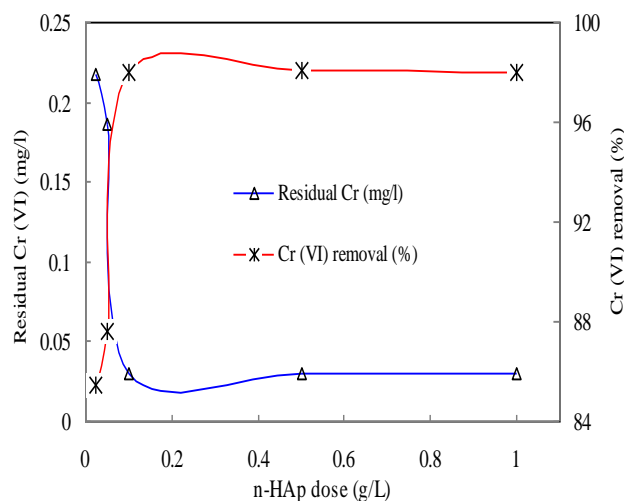


Figure 2: The influence of nano hydroxyapatite (n-HAp) dosage on hexavalent chromium (Cr (VI)) removal

Table 1 represents the results of the effects of contact time and Cr (VI) concentration on the adsorption. Based on data illustrated in Table 1 adsorption capacity of chromium increased for all three concentrations by increasing contact time to 30 min. At the contact time more than 30 min, the adsorption capacity had not significant changed. As shown in Table 1, increasing initial Cr (VI) concentration led to increase of q_e (mg/g) from 0.36 to 0.8 mg/g, 0.5 to 1.2 and 0.52 to 1.23 for initial chromium concentrations of 1, 1.5 and 2 mg/L, respectively when contact time increase from 10 to 30 min.

Table 1: The influence of Hexavalent chromium (Cr (VI)) concentration on its adsorption capacity by nano hydroxyapatite (n-HAp) as a function of contact time

Contact time (min)	n-HAp adsorption capacity (mg/g)		
	Cr (VI) concentration (1 mg/L)	Cr (VI) Concentration (1.5 mg/L)	Cr (VI) Concentration (2 mg/L)
10	0.36	0.50	0.52
20	0.56	0.74	0.86
30	0.80	1.20	1.23
40	0.81	1.21	1.23
50	0.81	1.21	1.24

To evaluate the kinetics of Cr (VI) adsorption onto n-HAp powders, eight of the most used kinetic models (pseudo-first order, pseudo-second order, zero order, first order, second order, fractional power, Elovich and intraparticle diffusion) were fitted to experimental re-

sults^{17,20}. The values of constants of kinetic models like pseudo-first order, pseudo-second order, zero order, first order, second order, Elovich, fractional power and intraparticle diffusion^{21,22} for sorption of Cr (VI) on n-HAp powders is given in Table 2.

Table 2: Kinetic parameters of Hexavalent chromium (Cr (VI)) adsorption onto nano hydroxyapatite (n-HAp)

Kinetic models	Cr (VI) concentration (mg/L)											
	1				1.5				2			
	R ^{2a}	SSE ^b	q _{e,cal} ^c (mg/g)	Constants	R ²	SSE	q _{e,cal} (mg/g)	Constants	R ²	SSE	q _{e,cal} (mg/g)	Constants
Pseudo-first order k _{1p} (min ⁻¹)	0.97	0.89	1.93	0.086	0.98	0.99	3.70	0.129	0.98	1.5	1.13	0.128
Pseudo-second order k _{2p} (g/ mg min)	0.99	0.09	0.99	0.022	0.99	0.08	1.24	0.010	0.98	0.09	1.36	0.007
Zero order k ₀	0.94	50	0.38	0.001	0.84	65	0.57	0.010	0.86	69	0.63	0.021
First order k ₁ (1/min)	0.88	5	0.93	0.027	0.82	8	0.57	0.024	0.81	12	0.46	0.023
Second order k ₂ (g/ mg min)	0.80	1	0.39	0.048	0.77	1.6	0.55	0.031	0.75	2	0.61	0.028
Fractional power K v	0.98	2.6	-	0.050 0.711	0.93	4.4	-	0.115 0.632	0.95	4.8	-	0.125 0.639
Elovich α _E (mg/g min) β _E (g/mg)	0.98	5.7	-	2.238 0.432	0.93	6.7	-	1.945 0.514	0.95	6.8	-	1.744 0.573
Intra-particle diffusion k _p (mg/(g min ^{0.5}))	0.96	3.7	-	0.211	0.89	3.8	-	0.139	0.14	3.9	-	0.148

^a Correlation coefficient

^b Sum of squared errors

^c Calculated adsorption capacity

As seen in Table 2, pseudo-second order has the highest correlation coefficients (R²). In addition, as indicated in Table 2, the SSE of the pseudo-second order model is less than other mentioned kinetic models²³. This result indi-

cates that the pseudo-second-order model was fitted well to experimental data.

To examine the specific relationship between sorption and the concentration of sorbate at equilibrium and to determine of maximum

capacity of sorbent, various isotherm models have been employed for fitting the data. So, to describe the chromium uptake capacity and its adsorption behavior onto n-HAp powders, isotherm data obtained were fitted by three isotherm including Langmuir, Freundlich and Dubinin-Radushkevich (D-R)¹⁸.

Table 3 shows the isotherm constants, correlation coefficient (R^2) and $\Delta_g(\%)$ for Cr (VI) adsorption onto n-HAp powders. As demonstrated in Table 3, compared to the other adsorption models, Langmuir isotherm model fits

to adsorption of Cr (VI) onto n-HAp well, in terms of the highest values of R^2 and lowest value of $\Delta_g(\%)$. This result suggest that the adsorption of Cr (VI) occurred on a monolayer of n-HAp surface and all molecules had equal activation energy²³. The favorability of the Langmuir model was further evaluated by the equilibrium dimensionless parameter R_L ($R_L=1/(1+bC_0)$), which was derived from the Langmuir model. As shown in Table 3, the values of R_L for Cr (VI) adsorption onto n-HAp powders are between 0 and 1.

Table 3: Fitted isotherm models for hexavalent chromium (Cr (VI)) adsorption onto n-HAp

Isotherms	Unit	Information
Freundlich model :Fitted model		$\ln q_e = 1.864 + 0.746 \ln C_e$
K_F	(mg/g(L/mg) ^{1/n})	6.450
N	-	1.340
R^2	-	0.983
$\Delta_g(\%)$	-	53
Langmuir model: Fitted model		$C_e/q_e = 0.133 + 0.458 C_e$
K_L	L/mg	3.450
R_L	-	0.126
Q_{max}	mg/g	2.180
R^2	-	0.998
$\Delta_g(\%)$	-	5
D-R :Fitted model		$\ln q_e = 1.218 - 0.0021 \epsilon^2$
E	kJ/mol	15.430
K_{DR}	mol ² /kJ ²	0.002
R^2	-	0.971
$\Delta_g(\%)$	-	67

Discussion

As Figure 1 illustrate, the results show that Cr (VI) adsorption onto n-HAp considerably affected by pH values. The reason that n-HAp behaved differently in adsorbing Cr (VI) at different solution pHs can be explained with considering the pH_{pzc} of the adsorbent as well as molecular nature of Cr (VI). The pH_{pzc} of n-HAp powders was found about 7.8. This means that n-HAp powders surface was negatively charged at solution pH above 7.8 and chromium ions were repelled by n-HAp powders surface resulting in the reduction of Cr (VI) adsorption. At pH higher than pH_{pzc} , the surface of n-HAp powders can be deprotonated¹⁸.

Therefore, in the elevated range of pH, the surface charge of n-HAp powders is negative

and at pH values below the pH_{pzc} , the surface of n-HAp powders was positively charged¹⁶, causing better Cr (VI) ions adsorption through the electrostatic attraction. According to the solubility equilibrium of chromium in acidic conditions (pH=2-3), $HCrO_4^-$ is predominant species of Cr (VI). As the pH increases, CrO_4^{2-} become the dominant form of chromium^{1,9,23}. At pH below the pH_{pzc} , the surface charge of n-HAp powders was positive¹⁶. Therefore, Cr (VI) through electrostatic attraction and/or via the binding of $HCrO_4^-$ to acidic functional groups on the surface of n-HAp is adsorbed. In addition, the number of protons available on the surface of the adsorbate increases when the pH of the solution become less than the pH_{ZPC} , which this condition causes to increase of the removal efficiency (%). Similar results for relation between Cr (VI) adsorption from aqueous

solution and pH values have been reported in other research^{1,21}.

Because adsorption processes is mainly a surface phenomenon, therefore, adsorption efficiency can significantly affect by surface area and available active sites due to the amount the mass of adsorbent^{23,24}. The results of removal of chromium (%) at various n-HAp doses indicated (Figure 2) that the removal of chromium with increase in n-HAp concentration from 0.025 to 0.1 g/L. However, the elevation of n-HAp powders dosage beyond this value was not effective significantly on Cr (VI) adsorption. This phenomenon can be explained by some reasons. One possible reason could be due to overlap of active sites at higher adsorbent masses resulting in reduced effective surface area required for sorption. The other possible reason for this phenomenon is that some of active adsorption sites may remain unsaturated^{1,23}. Based on this result, it can be concluded that 0.1 g/L of n-HAp powders is the optimum mass of this sorbent for Cr (VI) elimination from water. These findings are similar to other researchers' work, that showed an increase in the concentration of adsorbent followed by an increase in chromium removal efficacy^{1,25,26}.

As showed in Table 1, for all of the of initial Cr (VI) concentration, the removal of Cr (VI) increased as an increase concentration. At the contact time further 30 min, because of the constant mass of n-HAp powders for all three concentrations, the adsorption capacity had not significant changed due to limited adsorption sites. Increasing of q_e (mg/g) with elevation of initial Cr (VI) concentration may related to driving forces that need to overcome the resistances of pollutants migration from the aqueous solutions to n-HAp powders surface. Similar results were found in previous researches^{24,27}.

The value of the correlation coefficient (R^2) and SSE (Table 2) indicated that the adsorption data for Cr (VI) onto n-HAp best fit the pseudo-second-order model. The basic assumption behind the pseudo-second-order model, indicate that chemisorption plays a major role and may controls the adsorption process²⁸.

For the optimizing an operating procedure and designing of an adsorption system, the analysis of equilibrium data is important. It could be applied to develop an equation comparing different adsorbent under different operational conditions. The Langmuir adsorption model is probably the well-known theoretical treatments of non-linear sorption^{23,18,29}.

The value of R_L in Langmuir represents the adsorption situations to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($R_L < 1$) or irreversible ($R_L = 0$)¹⁸. Based on the R_L values shown in Table 3, the results confirm the favorability of Cr (VI) adsorption onto n-HAp powders.

Analysis of data with D-R isotherm showed that the energy of Cr (VI) adsorption process onto n-HAp powders was 15 kJ/mol. It indicates that chemical adsorption is the dominant process under the experimental conditions, which is in agreement with the data obtained from kinetic study^{1,18,23}.

Conclusion

The present study attempted to reveal that the n-HAp is an ecofriendly and effective adsorbent for the removal of Cr (VI) from aqueous solution. The size of the synthesized powder was about 53 nm and it had a BET surface area of 100 m²/g. pH_{pzc} of n-HAp was 7.8. The adsorption process was influenced by the pH medium and the optimum pH was 7. The kinetic studies showed that the pseudo-second order model were fitted well to adsorption data under selected condition ($R^2 > 0.998$). Furthermore, the isotherm equilibrium studies confirmed that the Langmuir model is the best model for the adsorption process of Cr (VI) by n-HAp. Adsorption capacity of Cr (VI) was 2.18 mg/g, and optimal dosage of n-HAp was 0.1 g/L. Analysis of our experimental data with D-R isotherm showed that adsorption of Cr (VI) onto n-HAp was chemisorption in nature. In a word, Cr (VI) adsorption onto n-HAp was an affordable and simple process for treating polluted Cr (VI) water.

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Conflict of interest statement

The authors have no conflict of interests to declare.

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