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#### **Original Article**

# 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 to11), 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

S ince heavy metals are not biodegradable and tend to accumulate in organisms, they are very toxic<sup>1-5</sup>. 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<sup>4,6</sup>. 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<sup>4,6,7</sup>. 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 water<sup>6-8</sup>. Based on these standard, the maximum concentration level of Cr (VI) in drinking water should not excess 0.05 mg/l<sup>1,6</sup>. 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 techniques<sup>9</sup>.

Several techniques have been investigated for the removal of Cr (VI) from water<sup>10</sup>. 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 well<sup>11</sup>. Different sorbent have been used for the elimination of the Cr (VI) from water and waste streams<sup>9,11</sup>. 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 water<sup>12</sup>. 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 users<sup>12-17</sup>.

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<sup>12,15</sup>. Briefly, the manufacture of n-HAp involved the initial formation of 0.5 M Ca (OH)<sub>2</sub> 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 1-2drops 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  $Ca_{10}PO_4(OH)_2$ powder. Finally, The  $Ca_{10}PO_4(OH)_2$  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):

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

where k is a constant,  $\lambda$  is the x-ray wavelength,  $\beta$  is the line broadening at half the maxwww.SID.ir imum intensity in radians, and  $\theta$  is the Bragg angle, respectively<sup>16</sup>.

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 study<sup>18</sup>.

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  $K_2Cr_2O_7$  in 1.0 L of distillated 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 methods<sup>19</sup>.

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

$$RE(\%) = \left(\frac{C_{ini} - C_t}{C_{ini}}\right) \times 100 \ (2)$$
$$q_e = \frac{V}{M} \times (C_{ini} - C_t) \ (3)$$

where,  $C_{ini}$  and  $C_i$  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)<sup>18</sup>. Apart from the correlation coefficient (R<sup>2</sup>), the applicability of the isotherm equations is quantitatively judged by comparing a normalized deviation  $\Delta_g(\%)$ , which can be described as:

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

where  $q_{e,exp}$  is observed from the batch experiment,  $q_{e,cal}$  is estimated from the isotherm for corresponding  $q_{e,exp}$ , and n is the number of measurements in experimental isotherm. The smaller of  $\Delta_g(\%)$  value indicates the better isotherm fitting<sup>20,21,22</sup>. Apart from the correlation coefficient (R<sup>2</sup>) 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:

$$SSE = \sum \frac{(q_t, e_{xp} - q_{t,cal})^2}{q^2_{t,exp}}$$
(5)

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

In this study, the Langmuir isotherms were chosen to determine the maximum adsorption capacity corresponding to the complete monolayer coverage on n-HAp<sup>23</sup>. The linear form of the Langmuir isotherms is represented by the following equation:

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

In the Langmuir equations,  $Q_{max}$  (mg/g) and b are constant and can be determined from the slope and intercept<sup>18</sup>.

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 molecules<sup>1</sup>. 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:  $\ln q_e = \ln Q_{\max} - K_{DR} \varepsilon^2 \ (8)$ 

In the D-R model,  $\varepsilon$  (Polanyi potential) is RT ln(1+1/Ce), Q<sub>max</sub> is the adsorption capacity (mg/g), K<sub>DR</sub> is a constant related to adsorption energy and finally R and T are the gas constant and temperature (K<sup>0</sup>), respectively<sup>1</sup>. The value of K<sub>DR</sub> (mol<sup>2</sup>/(kJ<sup>2</sup>)) can be calculated from the slope of the plot of lnq<sub>e</sub> versus  $\varepsilon^2$ , and Q<sub>max</sub> (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 m<sup>2</sup>/g. The pH <sub>pzc</sub> 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 concentration 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.

	n-HAp adsorption capacity (mg/g)								
Contact time (min)	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						

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

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 results<sup>17,20</sup>. 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<sup>21,22</sup> 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)

	Cr (VI) concentration (mg/L)											
	1				1.5				2			
Kinetic models	R <sup>2a</sup>	SSE <sup>b</sup>	q <sub>e<sup>9</sup>cal</sub> c (mg/g)	Constants	R <sup>2</sup>	SSE	<b>Q</b> e <sup>9</sup> cal (mg/g)	Constants	$\mathbf{R}^2$	SSE	<b>q</b> e, ca l (mg/g)	Constants
<b>Pseudo-first orde</b> k <sub>1p</sub> (min <sup>-1</sup> )	r 0.97	0.89	1.93	0.086	0.98	0.99	3.70	0.129	0.98	1.5	1.13	0.128
<b>Pseudo-second or</b> k <sub>2p</sub> (g/ mg min)	<b>der</b> 0.99	0.09	0.99	0.022	0.99	0.08	1.24	0.010	0.98	0.09	1.36	0.007
<b>Zero order</b> $k_0$	0.94	50	0.38	0.001	0.84	65	0.57	0.010	0.86	69	0.63	0.021
<b>First order</b> k <sub>1</sub> (1/min)	0.88	5	0.93	0.027	0.82	8	0.57	0.024	0.81	12	0.46	0.023
<b>Second order</b> k <sub>2</sub> (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
<b>Fractional power</b> 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
<b>Elovich</b> $\alpha_E (mg/g min)$ $\beta_E= (g/mg)$	0.98	5.7	-	2.238 0.432	0.93	6.7	-	1.945 0.514	0.95	6.8	-	1.744 0.573
<b>Intra-particle diff</b> k <sub>p</sub> (mg/(g min <sup>0.5</sup> ))	f <b>usion</b> 0.96	3.7	-	0.211	0.89	3.8	-	0.139	0.14	3.9	-	0.148

<sup>a</sup> Correlation coefficient

<sup>b</sup> Sum of squared errors

° Calculated adsorption capacity

As seen in Table 2, pseudo-second order has the highest correlation coefficients ( $\mathbb{R}^2$ ). In addition, as indicated in Table 2, the SSE of the pseudo-second order model is less than other mentioned kinetic models<sup>23</sup>. 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-Radushkuvich  $(D-R)^{18}$ .

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 energy<sup>23</sup>. 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 f	or hexa	valent	chromium	(Cr	(VI))	adsorption	onto n-HA	۱p
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Isotherms	Unit	Information
Freundlich model :Fitted model		lnq <sub>e</sub> =1.864+0.746 lnCe
$K_{\rm F}$	$(mg/g(L/mg)^{1/n})$	6.450
N	-	1.340
$\mathbf{R}^2$	-	0.983
$\Delta_{\rm g}(\%)$	-	53
Langmuir model: Fitted model		$Ce/q_e = 0.133 + 0.458 Ce$
K <sub>L</sub>	L/mg	3.450
R <sub>L</sub>	-	0.126
Q <sub>max</sub>	mg/g	2.180
$\mathbf{R}^2$	-	0.998
$\Delta g(\%)$	-	5
D-R :Fitted model		$Inq_e = 1.218 - 0.0021 \epsilon^2$
E	kJ/mol	15.430
K <sub>DR</sub>	$mol^2/kJ^2$	0.002
$\mathbf{R}^2$	4	0.971
$\Delta g(\%)$	-	67

## Discussion

As Figure 1 1illustrate, 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<sub>pzc</sub> of the adsorbent as well as molecular nature of Cr (VI). The pH<sub>pzc</sub> 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<sub>pzc</sub>, the surface of n-HAp powders can be deprotonated<sup>18</sup>.

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 charged<sup>16</sup>, causing better Cr (VI) ions adsorption through the electrostatic attraction. According to the solubility equilibrium of chromium in acidic conditions (pH=2-3), HCrO<sub>4</sub><sup>-1</sup> is predominant species of Cr (VI). As the pH increases,  $CrO_4^{-2}$ become the dominant form of chromium<sup>1,9,23</sup>. At pH below the  $pH_{pzc}$ , the surface charge of n-HAp powders was positive<sup>16</sup>. 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<sub>ZPC</sub>, 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<sup>1,21</sup>.

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<sup>23,24</sup>. 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<sup>1,23</sup>. 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<sup>1,25,26</sup>.

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<sup>24,27</sup>.

The value of the correlation coefficient ( $\mathbb{R}^2$ ) 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 process<sup>28</sup>. 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<sup>23,18,29</sup>.

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 m<sup>2</sup>/g. pH<sub>pzc</sub> 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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#### References

- 1. Nemr AE. Potential of pomegranate husk carbon for Cr (VI) removal from wastewater: Kinetic and isotherm studies. *J Hazard Mater.* 2009;161:132-141.
- 2. Daneshvar N, Salari D, Aber S. Chromium adsorption and Cr (VI) reduction to trivalent chromium in aqueous solutions by soya cake. J Hazard Mater B. 2002;94:49-61.
- **3.** Costa M. Potential hazards of hexavalent chromate in our drinking water. *Toxicol Appl Pharmacol.* 2003;188:1-5.
- 4. Yas AR, Andelib A, Nuran DA. Adsorption of chromium on chitosan: Optimization, kinetics and thermodynamics. *Chem Eng J.* 2009;151:188-194.
- 5. Vikrant S, Pant KK. Removal of chromium from industrial waste by using eucalyptus bark. *J Hazard Mater*. 2006;97:15-20.
- 6. Gupta VK, Rastogi A, Nayak A. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. J Colloid and Interf Sci. 2010;342:135-141.
- 7. Nityanandi D, Subbhuraam CV,. Kinetics and thermodynamic of adsorption of chromium (VI) from aqueous solution using puresorbe. *J Hazard Mater*. 2009;70:876-882.
- Ramos Ramirez EG, Ortega NL, Contreras Soto C, Olguin Gutierrez MT. Adsorption isotherm studies of chromium (VI) from aqueous solutions using solgel hydrotalcite- like compounds. *J Hazard Mater*. 2009;172:1527-1531.
- **9.** Mohan D, Charles U. Pittman Jr. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water: a review. *J Hazard Mater B*. 2006;137:762-811.

- **10.** Wu XW, Ma H w, Zhang Y R. Adsorption of Chromium (VI) from solutions by a mesoporous alominisilicate synthesized from microcline. *Appl Clay Sci.* 2010;48:538-541.
- **11.** Narayanan NV, Ganesan M. Use of adsorption using granular activated carbon (GAC) for the enhancement of removal of chromium from synthetic wastewater by electrocoagulation. *J Hazard Mater.* 2009;161:575-580.
- **12.** Sairam Sundaram C, Viswanathan N, Meenakshi S. Defluoridation chemistry of synthetic hydroxyapatite at nano scale: Equilibrium and kinetic studies. *J Hazard Mater*. 2008; 155:206-215.
- **13.** Vega ED, Pedregosa J C, Narda G E, Morando PJ. Removal of oxovanadium (IV) from aqueous solutions by using commercial crystalline calcium hydroxyapatite. *Water Res.* 2003;37:1776-1782.
- **14.** Sandrine B, Ange N, Didier B. Eric C, Patrick S. Removal of aqueous lead ions by hydroxyapatite: equilibria and kinetic process. *J Hazard Mater*. 2007; 139:443-446.
- **15.** Sheha RR. Sorption behaviour of Zn (II) ions on synthesized hydroxyapatites. *J Colloid Interface Sci*. 2007;310:18-26.
- **16.** Jai Poinern GE, Malay KG, Ng YJ, Touma BI. T. Defuoridation behavior of nanostructured hydroxy-apatite synthesized through an ultrasonic and microwave conbined techniqe. *J Hazard Mater*. 2011. 185:29-37.
- 17. Qiu C, Xiao X, Liu R. Biomimetic synthesis of spherical nano-hydroxyapatite in the presence of polyethylene glycol. *Ceramics International*. 2008;34:1747-1751.
- 18. Ghanizadeh G, Asgari G. Adsorption kinetic and isotherm of methylene blue and its removal from aqueous solution using bone charcoal. *React Kinet Mech Catal.* 2011;102:127-142.
- **19.** American Public Health Association. *Standard methodes for the examination of water and wastewater*. 20<sup>st</sup> ed. Washington DC: APHA;1998.
- **20.** Faria P, Orfao JJM, Pereira MFR. Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. *Water Res.* 2004;38:2043-2052.
- **21.** Khambhaty Y, Mody K, Basha S,Jha B. Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine Aspergillus niger. *Chem Eng J.* 2009;145:489-495.
- **22.** Behnamfard A, Salarirad MM. Equilibrium and kinetic studies on free cyanide adsorption from aqueous solution by activated carbon. *J Hazard Mater*. 2009;170:127-133.

- **23.** Moussavi G, Barikbin B. Biosorption of chromium (VI) from industrial wastewater onto pistachio hull waste biomass. *Chem Engin J.* 2010;162:893-900.
- 24. Bansal M, Singh D, Garg VK. A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes' carbons. J Hazard Mater. 2009;171:83-92.
- **25.** Bansal M, Garg U, Singh D, Garg VK. Removal of Cr (VI) from aqueous solutions using pre-consumer processing agricultural waste: a case study of rice husk. *J Hazard Mater*. 2009;162:312-320.
- **26.** Rao M, Parwate A V, Bhole A G. Removal of Cr<sup>6+</sup> and N<sup>i2+</sup> from aqueous solution using bagasse and fly ash. *Waste Manage*. 2002;22:821-830.

- 27. Garg UK, Kaur M P, Garg V K, Sud D. Removal of nickel (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. *Bioresour Technol.* 2008;99:1325-1331.
- **28.** Abramian L, El-Rassy H. Adsorption kinetics and thermodynamics of azo-dye Orange II onto highly porous titania aerogel. *Chem Eng J.* 2009;150:403-410.
- **29.** Arami MY, Limaee N ,Mahmoodi NM. Investigation on the adsorption capability of egg shell membrane towards model textile dyes. *Chemosphere* 2006;65:1999-2008