Characterization of Cr(VI) Removal from Aqueous Solutions by Natural Hydroxyapatite from Bone Ash and Determination of Optimum Conditions

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Abstract
The aim of this paper is eliminating Cr(VI) by natural HAP. HAP is an inexpensive material which is used from bovine critical bone ash in order to remove heavy metal ions like Cr(VI). Some experiments in different pH are performed (pH = 2, 3, 7). Maximum adsorption was appeared at pH = 2, dosage = 0.3 gr, C0 = 10 mg/l. Cr(VI) removal depends on pH value and initial amount of Cr(VI) result of experiments were analyzed by Longmuir and Freundrich and kinetic model.

Keywords: Adsorption, Bone Ash, Cr Removal, Heavy Metal Ions, Kinetic Model, Natural Hydroxyapatite

1. Introduction
Heavy metals are harmful for human body and environment because they are toxic¹. So, they must remove from waste water². US - Environmental Protect Agency (EPA) and the World Health Organizations (WHO) improve their standards by drinking water. They mention the amount of Cr(VI) mustn't higher than 0.5 mg/l. by using different process toxic can be removed from water, such as chemical precipitation⁴, solvent extraction⁵, electrolytic processes⁶, reverse osmosis⁷, chemical oxidation or reduction⁸, ion exchange⁹ and adsorption¹⁰,¹¹. among this method absorption is more useful these years because it is more economic and efficient¹². Hydroxy apatite (N_HAP) with the formula is provided from cortical bone ash¹⁳, and it is a useful material in environment. HAP has some advantages which are mentioned such as eliminating of heavy metal ions, low water solubility, reducing and oxidizing¹⁶–²⁰. In this paper Cr(VI) was eliminated by N-HAP in different pH. Result of experiments were analyzed by longmuir and freundrich. In this study FTIR spectroscopy was used. FTIR is essential in changing functional groups. so it is shown changes in functional groups of Cr(VI).

2. Materials and Methods

2.1 Natural HAP Preparation
Hydroxyapatite
To produce N-HAP Spongy bones and cortical bones were eliminated. For burning organic material gas torch and direct flame is used. Then, clean bones were remained. This process got product which was contained char. Black powder which was places an air furnace at temperatures 600ºC to 1100ºC after getting cool the black ash transfer to a white granular powder this product is natural hydroxy apatite¹⁴.

2.2 Solutions
Double distilled water and the chromate solution was prepared from K₂Cr₂O₇ diluted in deionized water. Experiments with diffident pH values (pH = 2, 3, 5, 7) was performed. Multiline 330i pH-meter was used. In order

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to adjust the initial pH the 0.1M HCL, 0.1M NaOH were used.

2.3 Apparatus
Uv-visible spectrophotometer made by shimadzu company was used for determining the amount of Cr(VI) at $\lambda = 540$nm was used for analyzing Cr(VI) removal. To determine values of pH a multiline 330i pH-meter was used. The FTIR spectrometer used in this experiment, was Bomem SZM4404P model made in Canada.

2.4 Adsorption Studies
To determining the amount of Cr(VI) which was adsorbed on N-HAP the following equation is

$$q_e = (C_0 - C_e) \times \frac{V}{M}$$  \hspace{1cm} (1)

Where C0(mmol/L) is the initial Cr(VI) concentration and Ce is the equilibrium concentration of Cr(VI). V is mass of adsorbent (g) and m is volume solution (L), finally qe is the adsorption capacity per unit mass of N-HAP (mmol/g).

2.4.1 Adsorption Isotherms
A relation between the amount of sorption and the residual solute concentration are described by using some models for instance Longmuir and Freundrich.

2.4.1.1 Langmuir Isotherm
Longmuir is the most useful for monolayer absorption are a fixed number of absorption sites. There are as size as each other and there aren’t any interaction between them.

The linearized form of Langmuir isotherm is

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}b} + \frac{1}{q_{\text{max}}}Ce$$  \hspace{1cm} (2)

Where qm is the maximum adsorption capacity (mmol/g) and b is the Langmuir isotherm constants, according to Langmuir equation. Constants kL and qm can be evaluated from the plot of Ce/qe versus Ce.

The sorption of metal ions to N-HAP particles is optimized when the values are less than unity. The optimum range of RL, called separation factor, which estimates the degree of suitability that is shown by Table 1 and it can be obtained by the following equation:

$$RL = \frac{1}{1 + KL C_0}$$  \hspace{1cm} (3)

2.4.1.2 Freundlich Isotherm
Freundlich is a practical model for heterogeneous absorption and independent sites. There is no surface. Freundlich isotherm is expressed as:

$$q_e = KF Ce^n$$  \hspace{1cm} (4)

KF and 1/n constant were represented the absorption capacity. They depend on temperature. The logarithmic form can expressed as:

$$\ln q_e = \ln b + \frac{1}{n} \ln Ce$$  \hspace{1cm} (5)

The values of 1/n less than 1 represent a favorable adsorption. In our paper, we used these two isotherms.

2.4.2 Sorption Kinetics
The two main kind of sorption kinetic models were used to gain an appropriate rate equation and discover the controlling mechanism of process. The pseudo-first order is used for the liquid/solid system. In this model the surface changes rates is proportional to the remaining amount of surface sites. It is mentioned bellow:

$$\log (q_e - qt) = \log q_e - \left(\frac{1}{q_{\text{max}}} \cdot 0.303\right) t$$  \hspace{1cm} (6)

where qe and qt are the equilibrium amounts of adsorbed Cr(VI) and at time t per unit mass of biosorbent (mmol/g), respectively and k1 is the Lagergren rate constant of the first-order adsorption (min⁻¹).

The pseudo-second-order model is shown which the rate is proportional to the square surface sites. This is given as:

$$t \cdot \frac{qt}{q_e} = \frac{1}{k_2 q_{\text{max}}} + \frac{1}{q_e} t$$  \hspace{1cm} (7)

where k2 for the second-order adsorption kinetics is the rate constant (g/mmol/min).

<table>
<thead>
<tr>
<th>Table 1. Ranges of RL</th>
<th>Type of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL &gt; 1</td>
<td>unfavorable</td>
</tr>
<tr>
<td>RL = 1</td>
<td>Linear</td>
</tr>
<tr>
<td>0 &lt; RL &lt; 1</td>
<td>Favorable</td>
</tr>
<tr>
<td>RL &lt; 0</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>
3. Adsorption Thermodynamic Studies

There are some thermodynamic parameters such as standard enthalpy change ($\Delta H^\circ$), standard free energy ($\Delta G^\circ$) and standard entropy change ($\Delta S^\circ$). It can be expressed by:

$$K_e = \frac{q_e}{Ce}$$  \hspace{1cm} (8)

$$\Delta G^\circ = -RT\ln K_e$$  \hspace{1cm} (9)

$$\ln K_e = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$  \hspace{1cm} (10)

Thermodynamic experiments were performed at a 15°C to 55°C and the unit of temperature is kelvin (K).

4. Result

4.1 Determination of Optimum Operating Conditions

With six different kinds of solutions which have different dosages we examine the effect of N-HAP on the absorption efficiency (0.1g, 0.2g, 0.3g, 0.5g, 1g, 3g). The results are shown in Figure 1. They are shown that equilibrium concentration is decreased. On the other hand chromium ion is increased. They can occupy only a certain amount of active sites if the initial Cr(VI) is constant. So, the amount of absorption ions do not change by increasing the number of active sites.

4.2 Adsorption Studies Results

First we added 0.2g of N_HAP to the Cr solution (200 ml) with three different pH values, then poured it in to a flax with the speed of 300rpm. The amount of absorption is examined in different time 5, 10, 15, 30, 60, 120, 240, 480, 720, 960 minutes. The efficiency of eliminating Cr ion in given as:

$$K_d = \frac{\text{amount of Cr in adsorbent}}{\text{amount of Cr}}$$  \hspace{1cm} (11)

$$C(\%) = \frac{C_0 - Ce}{C_0} \times 100$$  \hspace{1cm} (12)

Where $C_0$ and $Ce$ are the initial and final equilibrium concentrations (mmol/g), $m$ is the weight of the adsorbent (g) and $v$ is the volume of the solution (mL). This equation can be described as follows:

removal efficiency (%) = 100 $K_d$ \hspace{1cm} (13)

Equilibration time is 24h. The metal ions which were absorbed was computed by substituting final concentration instead of initial concentration finally, Langmuir isotherm was shown in Figure 2. KL, qm constants were given in Table 2. RL amount with initial Cr(VI) was given in Figure 3. Freundrich isotherm was shown in Table 3. The linear relations between Ln(qe) and Ln(ce) was given in Figure 4. 1/n amount was shown in Figure 4.

![Figure 1. Equilibrium concentrations as a function of dose of N-HAP.](image)

![Figure 2. Langmuir isotherm model for natural HAP particles.](image)
This shows, in less pH the absorption is better.

### 4.3 Kinetic Studies

The kinetic highest studies absorption of N-HAP was happened in pH = 2, Figure 5 was shown 80% of efficiency. The absorption of commercial HAP was less than the absorption of N-HAP.

### 4.4 Thermodynamic Studies

The amount of $\Delta H$, $\Delta S$ were given in Figure 8 and Table 6. $\Delta G$ is negative, $\Delta H$ is positive, these shows that this reaction is endothermic.

$\Delta S$ is positive, if shows the rise of randomness.

Difference in amount of adsorption happen because of two reasons:

1) Using natural HAP instead of commercial HAP
2) Using different dosages of N-HAP in comparison to commercial HAP

The values of $k_1$ can be found with the plot log $q_e$-qt vs time. $k_2$ and $q_e$ were obtain from plots $t/qt$ vs $t$ as the slopes and intercepts of plots. From Figure 6 and Figure 7, the conclusions obtained for the adsorption of Cr(VI) ion to Equations. (6) and (7), and

<table>
<thead>
<tr>
<th>pH</th>
<th>$q_m$</th>
<th>b</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.4684</td>
<td>0.0445</td>
<td>0.984</td>
</tr>
<tr>
<td>3</td>
<td>1.3315</td>
<td>0.03457</td>
<td>0.991</td>
</tr>
<tr>
<td>7</td>
<td>1.222</td>
<td>0.002562</td>
<td>0.99</td>
</tr>
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</table>

Table 2. The langmuir constants for adsorption of chromate ions on N-HAP.

Figure 3. Plot of RL versus initial Cr(VI) concentration (M = 0.3 g, V = 50 mL).

<table>
<thead>
<tr>
<th>pH</th>
<th>$K_f$</th>
<th>$B_f$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.06241</td>
<td>0.942</td>
<td>0.999</td>
</tr>
<tr>
<td>3</td>
<td>0.04398</td>
<td>0.967</td>
<td>0.999</td>
</tr>
<tr>
<td>7</td>
<td>0.0305</td>
<td>0.957</td>
<td>0.999</td>
</tr>
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</table>

Table 3. Freundlich isotherm constants for adsorption of Cr(VI) ions onto N-HAP.

Table 4. RL for initial concentration of 0.1 mmol/l

<table>
<thead>
<tr>
<th>pH</th>
<th>RL</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 2.00</td>
<td>0.918</td>
</tr>
<tr>
<td>pH = 3.00</td>
<td>0.935</td>
</tr>
<tr>
<td>pH = 7.00</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Figure 4. Freundlich isotherm model for N-HAP.

Figure 5. Removal efficiency of N-HAP.
an approximate linear fit was appeared. The values of \( k_1, k_2 \) and \( R^2 \), represented in Table 5, indicate the pseudo second-order model show better correlation coefficients than the pseudo first-order model, which indicates this system of adsorption is not a adsorption.

**Table 5.** Pseudo-first and second order rate constants for adsorption of chromate ions onto N-HAP

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>( R^2 ) (1/min)</th>
<th>( k_1 )</th>
<th>( R^2 )</th>
<th>( k_2 ) (g/mmol.min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural HAP</td>
<td>0.990</td>
<td>0.0017</td>
<td>0.996</td>
<td>0.079</td>
</tr>
</tbody>
</table>

**5. Conclusion**

In this paper, the amount of Cr(VI) was eliminated by using N_HAP. N-HAP which was provided by cortical bones ash. Different behavior of chromate ion under various conditions were examined.

Following results are given:

1) Maximum absorption happen by decreasing pH (pH = 2.00)
2) The reaction follows the second order rate kinetics.

**Figure 8.** The plots of \( \ln K_e \) versus \( 1/T \) for the adsorption of the Cr(VI) on N-HAP.

**Figure 9.** Fourier transformed infrared spectra: a comparison between main functional groups of A = N-HAP before Cr adsorption and B = N-HA after Cr adsorption.
3) Freundlich isotherm is better than longmuir.
4) ΔG is negative and the reaction is spontaneous.
5) The amount of ΔH, ΔS shows that the reaction is endothermic.
6) Changing of functional group shows that chromate ion is absorbed.

6. References


