Adsorption of Hexavalent Chromium Ion from Aqueous Solution by Sodium Alginate and Carboxymethyl Cellulose Beads: Kinetics and Isotherm Studies

Ali J. Salim
Department of Chemistry, College of Science, Al-Mustansiriya University, Baghdad-Iraq.
E-mail: Alijs82@yahoo.com.

Abstract
The removal of hexavalent chromium from aqueous solutions using biopolymeric beads of crosslinked sodium alginate (SA) and carboxymethyl cellulose (SCMC) as the adsorbent is reported in this paper. The biopolymeric alginate and carboxymethyl cellulose beads were prepared and characterized by FTIR spectra. The studies of adsorption of Cr(VI) were conducted by varying various parameters: such as contact time, pH, amount of adsorbent and concentration of adsorbate. A comparison of kinetic models applied to the adsorption of Cr(VI) ions on the adsorbents was evaluated for the pseudo-first-order, the pseudo second-order and intraparticle diffusion kinetic models respectively. Results show that the pseudo second-order kinetic model was found to correlate the experimental data well. The experimental equilibrium data were applied to Langmuir and Freundlich isotherm models and their equilibrium parameters were estimated.

Keywords: adsorption kinetic; carboxymethyl cellulose; sodium alginate.

Introduction
The heavy metal pollution is of great concern among the kinds of environmental pollution because of their high toxicity and other adverse effects on human health [1]. Heavy metals like chromium, copper, lead, zinc, mercury, cadmium etc. are present in waste water from several industries such as metal cleaning and plating baths, refineries, paper and pulp, tanning, dyes and pigments, wood preserving, glass, ceramic paints, catalysis chemical manufacturing etc. in which chromium (VI) is present from 5 to 220 mg/dm$^3$ which leave into environment [2-3].

Chromium can be released to the environment through a large number of industrial operation. Including metal finishing industry, iron and steel industries and inorganic chemicals production. There are various methods to remove Cr(VI) including chemical precipitation, membrane process, ion exchange, liquid extraction and electro dialysis [4]. But most of these methods have many disadvantages including incomplete metal removal, use of expensive equipment, and higher energy consumption adsorption remain the most economical of toxic metal ions from waste water [5].

The biosorption is the passive, nonmetabolic process of binding various chemicals on biomass, including physicochemical interactions, adsorption and ion-exchange. In the case of biosorption, ion-exchange is the most important mechanism that is realized by interaction between metal ions and active groups present in biopolymers. Thus by immobilization of biomass in a polymeric matrix that yields beads or granules with optimum size, mechanical strength, rigidity and porosity characteristics, the efficient removal of metal ions can be carried out. [6] The research for high biomass sorption is expected to improve the potential for the introduction of new materials, which are likely to be competitive and cost efficient for the sorption of metals. One of the most widely studied naturally occurring biopolymers are polysaccharide based biosorbents such as alginate and carboxymethyl cellulose (CMC) which have binding sites for divalent cations due to the presence of various functional groups within them. [7].

Sodium carboxymethyl cellulose (SCMC) is an important biopolymer due to its high degree of solubility in water, biocompatible, nontoxic and low cost [8]. SCMC has been widely used as thickening agent and stabilizing agent in industrial field [9]. Alginates have been used extensively in the food, cosmetics, pharmaceutical and biomedical industries for their gel forming properties in the presence of
multivalent cations [10]. Alginites can make a gel in the presence of divalent and trivalent cations including Ca^{2+} and Al^{3+}. It has been shown that the exchange of the sodium ions from the guluronic acids with divalent ions, and the stacking of these guluronic groups, form a so-called egg-box structure [11].

The aim of this work was to study the adsorption of chromium (VI) from aqueous solution using sodium alginate and sodium carboxymethyl cellulose beads was investigated in this study the effect of factors such as contact time, initial concentration, pH, and adsorbent dose were investigated. Langmuir and Freundlich isotherms were evaluated and kinetics studied.

**Experimental**

**2.1- Material**

Sodium carboxymethyl cellulose and sodium alginate were purchased from sigma Aldrich and used as received, while aluminium chloride and potassium dichromate of analar grade from (BDH).

**2.2- Instrumentation**

Water bath shaker type lab companion BS-11, digital scale KERN-ABBS, UV-Visible spectrometer, CARY 100 con. pH meter type trans BP 300, shimadzu 8400 FTIR were employed in this work.

**2.3- Preparation of biopolymeric beads**

The polymer beads adsorbente were prepared by ionic gelation method by using aluminium chloride as cross-linking agent, prepared in two steps: in the first step. Aknown solution of a mixture of carboxymethyl cellulose (2g.) and sodium alginate (2g.) in 100ml. distilled water was added in to a 100ml. solution of 6% w/v of gelling agents solution with the help of asyring with constant stirring. The beads were removed after the gelation period of 30 min. using Millipore stainless steel sieve (pore size: 0.25mm) and washed with distilled water repeatedly to make it free from un-reacted ions. These biopolymeric beads were stored at room temperature and the swollen beads were used for the adsorption of Cr(VI).

**2.4- Adsorption experiments**

A stock solution of potassium dichromate of 1000mg/L was prepared. from these stock solution dilute concentrations of Cr(VI) was prepared by dilution of specified volume of stock solution 50ml of certain concentrations of Cr(VI) was stirred with certain amount of biopolymeric beads in water bath shaker for definite time interval. At the end of each adsorption experiment the solution was made alkaline at pH=12 and the residual Cr(VI) was determined using UV-Visible spectrophotometer [12]. For calibrating the UV-Visible spectrophotometer standard sample of dichromate was prepared and corresponding adsorption for each concentration was measured at $\lambda$ max 372nm. The removal percentage R% of Cr(VI) was calculated using the following equation.

$$R\% = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \quad \text{equation (1)}$$

Were, $C_i$ and $C_e$ are the initial and final concentration (mg/L) of Cr(VI).

**Adsorption and Kinetics Studies**

Effects of some selected reaction parameters on the rates of adsorption of Cr(VI) using the sodium alginate (SA) and sodium carboxymethyl cellulose (SCMC). The parameters considered include agitation time, adsorbent dosage, pH and initial concentration. To study the effect of agitation time on metal adsorption by SA, SCMC different contact durations (5,10,20,30,40,50 and 60 min) was tested. After each agitated time, the content of the bottle was filtered and the equilibrium concentration of each of the metals in the filtrate was determined.

The effect of adsorbent dosage, that is, the amount of SA, SCMC on the adsorption of metals was studied by adding 50 mL of the Cr(VI) to various amounts of the adsorbent (0.05 -0.5 g) in different plastic bottles covered and agitated by mechanical shaker.

The equilibrium time and the pH were kept constant during this test. To determine the effect of pH on the adsorption of Cr(VI), the pH of the wastewater was adjusted and maintained to the required value (1.0, 2.0, 3.0, 4.0, 5.0 and 6.0) with 0.1 M HCl and 0.1 M NaO\text{H} solution and mixed with the optimum
weight of the adsorbent and agitated at a preset equilibrium time. The adsorption capacity \( q_e \) was determined using the mass balance expression (Equation 2)[13].

\[
q_e = \frac{(C_i - C_e) \times V}{M} \quad \text{......................... (2)}
\]

Also, the adsorption capacity \( q_t \) at time \( t \) was determined using the Equation (3)[14].

\[
q_t = \frac{(C_0 - C_t) \times V}{M} \quad \text{......................... (3)}
\]

Where \( C_o \) is the initial metal ions concentration, \( C_e \) is the concentration of metal ions in solution (mg/L) at equilibrium, \( C_t \) is the concentration of metal ions in solution (mg/L) at time \( t \) in solution, \( V \) is volume of initial metal ions solution used (L) and \( M \) is mass of adsorbent used (g).

Furthermore, kinetics of adsorption was studied by analyzing the adsorptive uptake of Cr(VI) at different time intervals. The pseudo – first – order, pseudo – second – order and Intrapartical Diffusion model equations were fitted to the kinetics of adsorption Cr(VI) onto SA,SCMC. The linearity of each model, when plotted, was used to find out how suitable each model illustrate the adsorption.

### Adsorption Isotherm

Adsorption isotherm experiments were carried out at different temperatures (25,35,45)ºC by shaking the biopolymer beads (0.2g) with 50ml of Cr(VI)10,20,30,40,50 and 60 mg/L solution for 60 minutes at pH 2. The amount of Cr(VI) adsorbed onto the biopolymer beads.

3. Result and Discussion

3.1. FTIR spectra

Fig. (1), shows the FT-IR spectrum of the SCMC. The absorption peaks at 3313 and 3184 cm\(^{-1}\) were assigned to the stretching vibration of 2\(^{\circ}\) and 1\(^{\circ}\) O-H group respectively. The peak at 2916 cm\(^{-1}\) was due to the stretching vibration of aliphatic C-H. The absorption peaks at 1602 cm\(^{-1}\) is due to asymmetrical stretching vibration of COO\(^{-}\) groups. While the peak appear 1066 cm\(^{-1}\) is attributed to the C-O-C stretching vibration [15].

Fig.(2), shows the FT-IR of SA. The absorption peak at 3300 cm\(^{-1}\) represent the O-H stretching vibration, the peak at 2926 cm\(^{-1}\) was due to the stretching vibration of aliphatic C-H. The absorption peaks at 1606 cm\(^{-1}\) and 1421 cm\(^{-1}\) was due to asymmetric and symmetric stretching vibration of COO\(^{-}\)group [16]. While the peak appear at 1022 cm\(^{-1}\) was due to the stretching vibration of C-O-C group.

Fig.(1): FTIR Spectrum of SCMC beads.

Fig.(2): FTIR Spectrum of SA beads.

3.2. Effect of contact time

The amount of Cr(VI) adsorbed on SA and SCMC was studied as a function of shaking time. The results are given in Fig.(3). There was a rapid adsorption in the 40 minutes, then little change occurred with time. The percentage removal was 53.72% and 62.97% on to SA and SCMC respectively in the first 10 minutes. The percentage adsorption increased with increase the time and the percentage of removal Cr(VI) on SA and SCMC at 50 minutes reached 83.17% and 75.46% respectively.
3.3. Effect of pH

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. Fig. (4) shows the percentage of Cr(VI) removal as a function of pH. It is evident from this figure that the percentage adsorption is higher at lower pH. The maximum removal efficiency was 79.25% and 72.47% on SA and SCMC respectively. The best results were observed at pH 2.

In view of an electrostatic interaction between the sorbent–sorbate systems, it was decided to maintain the pH at 3.0 in further experiments. It was also observed that at the end of the adsorption experiments, pH of the solution increased from 3.0 to 5.5. This might be attributed to the protonation of amine group, HCrO₄⁻ reduction accompanied by H⁺ consumption, and slow release of alkalinity from the prepared sorbent [17].

3.4. Effect of adsorbent Dosage

Various amounts of SA, SCMC (0.05 to 0.5) g were exposed for a 60 min to 50ml of Cr(VI) solution with the concentration of 50 mg/L. Fig. (5) shows the removal efficiency of Cr(VI) against the amount of SA, SCMC used. The removal percentage increases by increasing of SA, SCMC amount. The percentage adsorption increased from 13.38% and 30% at lower adsorbent dose (0.05g) to 75.52% and 84.54 at higher adsorbent dose (0.5g) SA and SCMC respectively.

3.5. Effect of initial concentration

The effect of adsorbate ion concentration was studies by taking 10, 20, 30, 40, 50, and 60 mg/L with an optimum pH value, Fig. (6). The adsorption capacity increased with an increase in the initial Cr(VI) concentration. This is because an opportunity existed for increased reaction between the adsorbent and the adsorbate [18].
3.6. Adsorption kinetics modeling

The adsorption kinetic models are important in the process of removal of toxic heavy metals from the aquatic environment. In this study of a batch reaction, different reversible models were tested.

3.6.1. Pseudo-first order model

The pseudo-first order model is one of the most widely used procedures for the adsorption of a solute from an aqueous solution [19]. The pseudo-first order equation can be expressed as follows:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\] .......................... (4)

where \(q_t\) is the amount of metal ions adsorbed at time \(t\) (mg g\(^{-1}\)), \(q_e\) (mg g\(^{-1}\)) is equilibrium solid phase concentration and \(k_1\) is first order rate constant for adsorption(min\(^{-1}\)). The plot of \(\log (q_e - q_t)\) vs. \(t\) should result in a straight line. The rate constant can be calculated from the slope of the straight line (7).

![Fig.(7): First order plot of adsorption of Cr(VI) onto SA and SCMC.](image)

3.6.2. Pseudo-second order model

The pseudo-second order equation is based on the adsorption capacity of the solid phase. Contrary to other models, it predicts the behavior over the whole range of adsorption [20]. Pseudo-second order model based on the equilibrium adsorption capacity may be expressed in the form:

\[
\left( \frac{t}{q_t} \right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \] .......................... (5)

where \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is the rate constant of pseudo-second order adsorption. The plot of \(t/q_t\) vs. \(t\) should yield a straight line Fig.(8), which allows the computation of \(k_2\).

![Fig.(8): Second-order plot of adsorption of Cr(VI) onto SA and SCMC.](image)

3.6.3. Intra-particle diffusion

Intra-particle diffusion was explored using the intra-particle diffusion model given in Eq.(6).

\[
q_t = K_{dif} t^{1/2} \] .......................... (6)

where \(K_{dif}\) is the intra-particle diffusion rate constant and the meanings of the other terms have already been defined. This model predicts that the plot of \(q_t\) vs. \(t^{1/2}\) should be linear if intra-particle diffusion is involved in the sorption process Fig.(8). Intra-particle diffusion is the rate-controlling step if the line passes through the origin. [21]

![Fig.(9): Intrapartical Diffusion plot of adsorption of Cr(VI) onto SCMC and SA.](image)

The application of the different kinetic models unveiled some interesting features regarding the mechanism and rate-controlling...
step of the overall sorption process. The kinetic parameters of Cr(VI) onto SA and SCMC under different conditions were calculated and are given in Table (1). To quantify the applicability of each model, the correlation coefficient, $R^2$, was calculated for these plots. The linearity of these plots indicates the applicability of the three models. However, the correlation coefficients, $R^2$, showed that the pseudo-second-order model, fits better the experimental data ($R^2 \geq 0.9983$) than the pseudo-first-order and the intra-particle diffusion kinetic models Table (1) and Fig.(8,9).

While the linear curve of the second-order kinetic model were obtained when $t/q_e$ was plotted against time, for the adsorption of Cr(VI) onto SA and SCMC in Fig.(8). The results reveal that the second-order kinetic model well represents the experimental data for the adsorption of Cr(VI) onto SA and SCMC, this conclusion came from the good correlation coefficient obtained from second-order plot as well as the good match between the values of $q_e$(cal) and $q_e$(exp) [22].

### Table (1)

**Kinetic parameters for the adsorption of Cr (VI) onto SA and SCMC.**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>SA</th>
<th>SCMC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pseudo-first-order model</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_1 / 10^{-2}$ min$^{-1}$</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.872</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (experimental), mg g$^{-1}$</td>
<td>3.185</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (kinetic plot), mg g$^{-1}$</td>
<td>2.578</td>
</tr>
<tr>
<td></td>
<td>Pseudo-second-order model</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_2 / 10^{-4}$ g mg$^{-1}$ min$^{-1}$</td>
<td>0.261</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (experimental), mg g$^{-1}$</td>
<td>3.185</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (kinetic plot), mg g$^{-1}$</td>
<td>3.162</td>
</tr>
<tr>
<td></td>
<td>Intra-particle diffusion model</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{diff} /$ mg g$^{-1}$ min$^{-1/2}$</td>
<td>0.2817</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9439</td>
</tr>
</tbody>
</table>

**Adsorption Isotherms**

Adsorption isotherm are essential for the description of how metal ion concentration will interact with the adsorbent surface and are useful to optimize the adsorbent for the removal of Cr(VI) ions. The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the sorption. Several isotherm equations are available and two important isotherm are selected in this study, which are namely the Langmuir and Freundlich isotherms.

**Langmuir isotherm**

Assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The linear form of Langmuir isotherm equation is given as

$$\frac{1}{q_e} = \left(\frac{1}{K_L Q_m}\right) \frac{1}{C_e} + \frac{1}{Q_m}$$

where $C_e$ is the equilibrium concentration of the adsorbate (mg/L), $q_e$ is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), $Q_m$ and $K_L$ are Langmuir constants related to adsorption capacity and rate of adsorption [23] The Langmuir plots for the Cr(VI) adsorption by SA and SCMC is given in Fig.(10) from values of $R^2$ the langmiur isotherm is not applicable.
The linear form of Freundlich isotherm (24) is represented by the equation

\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \]  

(8)

where Ce is the equilibrium concentration of the adsorbate (mg/L) and qe is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g). Kf and n are Freundlich constants representing the adsorption capacity and intensity of adsorption respectively. The values of Kf and 1/n were obtained from the slope and intercept of the plot of \( \log q_e \) versus \( \log C_e \). The slope of \( 1/n \) ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [24]. Freundlich constants Kf and n are listed in Table (2). The Freundlich plots for the Cr(VI) adsorption by SA and SCMC is given in Fig.(11) from values of \( R^2 \) the freundlich isotherm is not applicable.

### Table (2)

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>langmiur</th>
<th>freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_m ) mg/g(^{-1})</td>
<td>( k_L ) Lmg(^{-1})</td>
</tr>
<tr>
<td>SCMC</td>
<td>7.56</td>
<td>0.02</td>
</tr>
<tr>
<td>SA</td>
<td>6.87</td>
<td>0.031</td>
</tr>
</tbody>
</table>

**Conclusion**

Biopolymeric beads of crosslinked carboxymethyl cellulose and sodium alginate proved to be an effective adsorbent for removal of Cr(VI) from aqueous solutions. The adsorption of Cr(VI) ion dependent on initial concentration of the metal ion, adsorbent dose, pH and contact time. The optimal condition for adsorption of Cr(VI) using SA and SCMC was pH 2, contact time 40 min and initial concentration 50 mg/L. The kinetics and isotherm studies indicated that the pseudo–first–order, pseudo–second–order, Intrapartical Diffusion, Langmuir and Freundlich model well described the adsorption equilibrium of Cr(VI) ion onto SA and SCMC .adsorption followed pseudo-second-order and Intrapartical Diffusion kinetics.

**Acknowledgment**

We are grateful to the ministry of higher education and scientific research for financial support of this work.
References


الخلاصة

في هذا البحث تم دراسة امتزاز أيون الكروم السداسي من محلوله المائي باستخدام بوليميرات حيوية محورة (صوديوم كاربووكسي ميثيل سيللوز، صوديوم الجنيت) باستخدام عامل التشابك كلوريد الألمنيوم. تضمن البحث دراسة العوامل المؤثرة على عملية الامتزاز: الدالة الحمضية، زمن التفاعل، كمية المادة المازة وتركيز أيون الكروم السداسي. كذلك تم دراسة حركة امتزاز أيون الكروم السداسي باستخدام: المعادلة الحركية من الدرجة الأولى الكاذبة، المعادلة الحركية من الدرجة الثانية الكاذبة ومعادلة الانتشار بين الجسيمات حيث وجد أن الدراسة تخضع للمعادلة الحركية الكاذبة من الدرجة الثانية. كذلك تم دراسة إيزوثيرمات الامتزاز باستخدام معادلة فريندليش ولانكماير وتبين أن الامتزاز لا يتبع كلا المعادلتين.