

# Modeling Chromium (VI) Biosorption by Acid Washed Crab Shells

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## Introduction

The removal of toxic heavy metals from the spent plating baths and the process rinse water is a growing concern for metal finishing industries. Among the pollutants, hexavalent chromium, such as chromate ( $\text{CrO}_4^{2-}$ ) is considered to be a serious toxic form, as it can easily cross the cell and nuclear membranes and cause genetic damage.<sup>1</sup> Niu and Volesky<sup>2</sup> proposed an acid washed crab (*ucides cordatus*) shell (AWCS) biosorption technique for effectively adsorbing anionic chromium (VI) species from aqueous solution. The acid washed crab shells in this work contain about 78% of chitin. Chitin is the world's second most abundant naturally occurring polysaccharide. Much of it is disposed of as waste from seafood crustaceans, mainly crabs, shrimps, prawns, and lobsters, where it occurs as a significant component in the shells/exoskeletons of these crustaceans.<sup>3</sup> Study on crab shells could provide important information for understanding similar waste biomaterials, such as shells of shrimps, prawns, lobsters and other chitin-containing biomaterials with regard to biosorption application. It was determined that chromium biosorption by AWCS was strongly affected by solution pH and ionic strength.<sup>2</sup> Chromate occurred in the forms of chromate and/or dichromate depending on the solution pH. Chromate or dichromate were mainly bound on the weak-base amino groups of chitin or protein present in AWCS.<sup>4</sup> These observations indicate that a mathematical model which can

effectively predict the chromium biosorption by AWCS has to be sensitive to parameters, such as solution pH, ionic strength, and chromium speciation. Earlier publications commonly used biosorption equilibrium models based on the Langmuir equation.<sup>5-7</sup> The equilibrium uptakes in this model were determined without reference to any of the important factors such as pH, ionic strength, and speciation of ions. As a result, the equilibrium constants are dependent on the solution conditions seriously limiting the prediction capability of these models over more extended sorption conditions.

Surface complexation modeling represents a body of knowledge that has been available for modeling of metal ion adsorption on various impenetrable surfaces.<sup>8</sup> These models have been developed to provide a way to describe the activity coefficient of both the surface species and the species in the solution. They can generally operate over a range of pH and ionic strength. The biosorbent AWCS used in this biosorption system was semipenetrable. While it is a popular biosorbent, unfortunately, the aforementioned model could not successfully describe the behavior of such a system. Developing a mathematical model that could effectively predict the biosorption behavior of semipenetrable biosorbents, such as crab shells and related biomaterials represents an outstanding challenge. In this work, a mathematical model was developed which was exemplified by chromium (VI) biosorption system. The model effectively represented the influence of solution pH, ionic strength and chromium speciation on the equilibrium chromium uptake. The prediction capability of the model was demonstrated using the experimental data of chromium (VI) biosorption obtained by Niu and Volesky.<sup>2</sup>

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## Model Description

The key aspects of the model reported in this work are as follows:

1. Assume anion biosorption by weak base groups of biosorbents to be based on the acid-base neutralization reaction. Similar approach was used for organic acids adsorption by weakly basic adsorbents, and it enabled incorporation of the pH effect.<sup>9,10</sup>

2. Attribute the nonideality of the system to the liquid phase. This is adequate for biosorption systems with low to medium ionic strength as has been confirmed by the results in this work and the results on cationic uranium biosorption by *Sargassum*.<sup>11</sup>

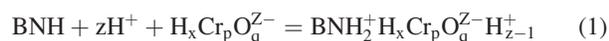
3. Consider the speciation of chemicals in the system. This makes it possible to consider different contributions of anionic species in solution to the uptake which is important when chemical speciation occurs.<sup>11</sup>

The model is applicable to biosorption or similar adsorption systems involved in anion sequestration by sorbents containing weak base such as amino or phenol groups. It is sensitive to and allows consideration of the effects of the pH, ionic strength and chemical speciation. In the case where there is no multiple speciation of the sorbate in the solution, the model is still applicable by only considering the uptake of one chemical species of interest. No model incorporating all of the aforementioned aspects had been reported for anion biosorption system so far.

The performance of the model was demonstrated with the AWCS-chromate biosorption system as shown in the following example.

## Anionic Species Binding

Anionic chromium (VI) species was adsorbed by the neutralization reaction with the positively charged protonated weak-base amino groups on the AWCS, shown in Eq. 1. This was based on the previously experimental evidence that the major functional groups responsible for chromium (VI) species binding were amino groups on AWCS.<sup>4</sup>



where BNH and  $\text{BNH}_2^+\text{H}_x\text{Cr}_p\text{O}_q^{z-}\text{H}_{z-1}^+$  represent the free weak-base amino groups on AWCS and adsorbed anionic chromium species, respectively. B represents biomaterial AWCS.  $\text{H}_x\text{Cr}_p\text{O}_q^{z-}$  denotes the anionic chromium species in the solution, p, q and x represent the number of chromium, oxygen and protons per chromium species, respectively. z symbolizes the charge.

Attributing all nonideality to the liquid phase, the activity of each species on the AWCS could be replaced by the corresponding concentration term, and that in the solution by the concentration term and the respective activity coefficient, then the following equation is obtained from the mass action law

$${}^{ad}K_{\text{H}_x\text{Cr}_p\text{O}_q^{z-}} = \frac{[\text{BNH}_2^+\text{H}_x\text{Cr}_p\text{O}_q^{z-}\text{H}_{z-1}^+]}{[\text{BNH}]\{\text{H}^+\}^z[\text{H}_x\text{Cr}_p\text{O}_q^{z-}]\gamma_{\text{H}_x\text{Cr}_p\text{O}_q^{z-}}} \quad (2)$$

{ } represents the activity of the species and [ ] represents the species concentration, (mol/g dry weight of biosorbents) for

surface species and (mol/L) for liquid species. The concentration of Cr species on the surface is also called uptake. The total Cr uptake is the sum of the Cr in different species adsorbed on the adsorbent.  $\gamma_{\text{H}_x\text{Cr}_p\text{O}_q^{z-}}$  is the activity coefficient of  $\text{H}_x\text{Cr}_p\text{O}_q^{z-}$  in the solution and  ${}^{ad}K_{\text{H}_x\text{Cr}_p\text{O}_q^{z-}}$  denotes the equilibrium constant of  $\text{H}_x\text{Cr}_p\text{O}_q^{z-}$  biosorption lumping activity coefficients of species on the solid phase ((mol/L)<sup>-(z+1)</sup>). Davies' equation<sup>12</sup> was used for calculating single ion activity coefficient in the liquid phase. The form of proton activity {H<sup>+</sup>} remains as could be obtained directly by pH measurement.

Similarly, the major interference anion Cl<sup>-</sup>, brought in the system by pH and ionic strength adjustment with HCl and NaCl,<sup>2</sup> was considered



$${}^{ad}K_{\text{Cl}} = \frac{[\text{BNH}_2^+\text{Cl}^-]}{[\text{BNH}]\{\text{H}^+\}[\text{Cl}^-]\gamma_{\text{Cl}^-}} \quad (4)$$

where  ${}^{ad}K_{\text{Cl}}$  is the Cl<sup>-</sup> equilibrium binding constant lumping activity coefficients of species on solid phase (L/mol)<sup>-2</sup>.  $\gamma_{\text{Cl}^-}$  represents the activity coefficient of Cl<sup>-</sup> in the solution and  $\text{BNH}_2^+\text{Cl}^-$  denotes the adsorbed Cl<sup>-</sup>.

## Mass Balance

The total anion binding capacity of the functional amino group [B<sub>T</sub>] (mol/g) equals to

$$[\text{B}_T] = [\text{BNH}] + \sum_i ([\text{BNH}_2^+\text{H}_x\text{Cr}_p\text{O}_q^{z-}\text{H}_{z-1}^+])_i + [\text{BNH}_2^+\text{Cl}^-] \quad (5)$$

where i represents the types of the chromium species, here referring to chromate and dichromate, respectively.

## Electroneutrality Condition

The electroneutrality condition is given by the following equation

$$[\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-] + \sum_i Z^*([\text{H}_x\text{Cr}_p\text{O}_q^{z-}])_i \quad (6)$$

Na concentration was assumed to be equal to the initial value, as it was found indifferent to chitin or protein.<sup>13</sup>

## Chromium (VI) Speciation

The anionic chromium species [ $\text{H}_x\text{Cr}_p\text{O}_q^{z-}$ ] in the earlier equations will be determined by the speciation of chromium (VI) in the solution. In the studied system at pH 2.0–3.6, the predominant species are  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ .<sup>2,4,14–16</sup> The pH range was based on the application conditions for anion biosorption with AWCS, because the major chemical functional groups on the chitin of AWCS are amide groups.<sup>4</sup> The logarithm of the proton dissociation constant of the positively charged protonated amide is 3.5.<sup>17</sup> The positive charge of the amide groups for anion binding is assured by their protonation upon adjusting the pH of the system in the desired range. In practice, for instance, the pH of nickel plating

wastewater containing chromium falls within this range.<sup>18</sup> The speciation of chromate is governed by the following equation:



The equilibrium constant  $K_{\text{Cr}}$  for the above reaction is  $10^{2.2} (\text{mol/L})^{-1}$ .<sup>14</sup> The equilibrium chromium concentration in the solution  $[\text{Cr}]$  (mol/L) is

$$[\text{Cr}] = [\text{H}_2\text{CrO}_4^-] + 2^*[\text{Cr}_2\text{O}_7^{2-}] \quad (8)$$

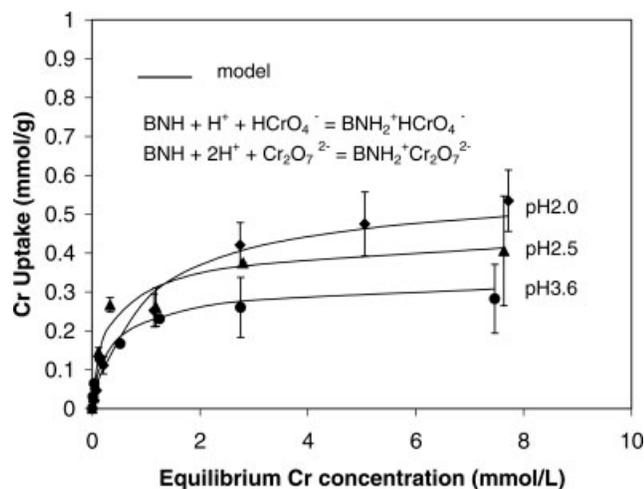
### Model Parameter Estimation

Model parameters  $B_T$ ,  ${}^{ad}K_{\text{H}_x\text{Cr}_p\text{O}_q^-}$  and  ${}^{ab}K_{\text{Cl}}$  were evaluated by fitting the earlier equations to the experimental data at pH 2.0–3.6 without NaCl addition,<sup>2</sup> and by minimizing the sum of the squared uptake residuals between the experimental data and model predicted values. When the model parameters were known, the model was used to predict the anionic chromium species biosorption at elevated ionic strength (0.1 M NaCl).

## Results and Discussion

### Modeling the pH effect on biosorption

Figure 1 illustrates Cr adsorption isotherms. The data points represent the experimental results obtained with a chromium oxide ( $\text{CrO}_3$ ) solution equilibrated with AWCS at pH 2.0–3.6 without NaCl addition.<sup>2</sup> The error bar stands for 95% confidence interval of the experimental data. The experimentally obtained uptakes were calculated by the mass balance of total Cr in the system. The initial and equilibrium total Cr concentration was determined by Inductively Coupled Plasma-Atomic Emission Spectrum.<sup>2</sup> The solid lines represent the model fitting curves. The model considering  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  binding accurately illustrates the trend of the pH effect on Cr isotherms, whereby Cr uptake was the highest at pH 2.0, and suppressed at higher pH values of 2.5 and 3.6. The correlation coefficient was 0.98 and the relative



**Figure 1. Modeling the effect of pH on chromium (VI) biosorption by AWCS.**

Experimental data were taken from the work of Niu and Volesky.<sup>2</sup>

residual was 4.4%. The regressed total capacity of AWCS for Cr binding came to 0.31 mmol/g, which is higher than that for *Zooglera ramigera*, *Rhizopus arrhizus*, and *Spirogyra*, and similar to that established for *Chlorella vulgaris*. However, it is lower than that for *Aeromonas caviae*, *Halimeda opuntia*, *Rhizopus arrhizus*, *Rhizopus nigrificans*, *Sargassum* and *Pinus sylvestris*.<sup>19</sup>

The regressed binding constant  $\log {}^{ad}K_{\text{Cr}_2\text{O}_7^{2-}} (\text{mol/L})^{-3}$  is 9.80,  $\log {}^{ad}K_{\text{HCrO}_4^-} (\text{mol/L})^{-2}$  is 7.29, and  $\log {}^{ad}K_{\text{Cl}^-} (\text{mol/L})^{-2}$  is 5.89. These values indicated the affinity of the studied anions that followed the decreasing sequence:  $\text{Cr}_2\text{O}_7^{2-} > \text{HCrO}_4^- > \text{Cl}^-$ . This confirms that the higher the charge and the bigger the size of the anion, the higher the affinity of the anion for the site.<sup>20</sup> The indication is in agreement with the fact that smaller ions have lower affinities for the sorbent active sites because of higher water hydration. The modeling results establish that the developed biosorption model effectively described the chromium (VI) species biosorption within the pH range of 2.0–3.6.

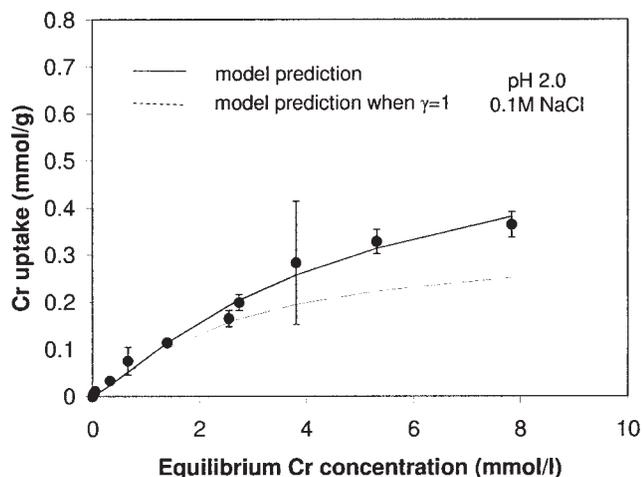
The comparison of the binding constants obtained in this work with those reported in the literature cannot be readily made because either modeling approaches or adsorption systems differ. For example, the logarithm of the binding constant of  $\text{HCrO}_4^-$  on the hydroxyl groups of goethite regressed from the surface complex model is 20.74.<sup>21</sup> This value is quite different from that obtained in this work as the model approach, and the adsorbents are different.

### Predicting the Ionic Strength Effect

The change of ionic strength influences adsorption by affecting the interfacial potential and therefore the activity of electrolyte ions.<sup>22</sup> Figure 2 shows the model prediction results on ionic strength effect. The data points are from chromium biosorption experiments at pH 2.0 and 0.1 M NaCl addition.<sup>2</sup> The solid line represents the model prediction curve. The model parameters used here were obtained from the model regression of chromium biosorption experimental data at pH 2.0–3.6 without NaCl addition in the previous section. The results showed that the developed model very accurately predicted the suppressed chromium uptake at ionic strength 0.1 M and pH 2.0. The relative residual is 5.1%.

However, when the nonideality in the liquid phase was neglected by setting the activity coefficient of solution species to 1 in the model, the prediction of such a model for Cr uptakes at ionic strength 0.1 M (the dashed line shown in Figure 2), deviates from the experimental data significantly as the chromium concentration increases.

Under the experimental conditions, the activity coefficients of the monovalent  $\text{HCrO}_4^-$  calculated by Davies' equation<sup>12</sup> are close to 0.8 at 0.1M NaCl, while that of the divalent ion  $\text{Cr}_2\text{O}_7^{2-}$  are significantly lower at 0.36. As the total chromium concentration in the solution increases, the percentage of  $\text{Cr}_2\text{O}_7^{2-}$  increases as well.<sup>14</sup> This may explain why the model prediction at the activity coefficient of solution species equaling to 1 greatly deviated from the experimental data at elevated chromium concentrations and ionic strength. These modeling results illustrated the rationality of considering the nonideality in the liquid phase by incorporating the activity coefficients of the solution species in the developed model.



**Figure 2. Model prediction of the ionic strength effect on chromium biosorption by AWCS.**

Experimental data were taken from the work of Niu and Volesky.<sup>2</sup>

Even though the obtained equilibrium constants in the current work are apparent in nature, as the surface nonideality is not accounted for, this modeling approach greatly simplifies the model calculations and adequately predicts the chromium (VI) biosorption experimental data at pH 2.0–3.6 with ionic strength up to 0.1 M.

The results showed that the developed model, capable of representing the influence of pH, ionic strength, chemical speciation and the interfering anion, overcomes the limitations of Langmuir equation, and appears adequate to describe and predict the behavior of biosorption systems containing both monovalent and multivalent species and semipenetrable biosorbent containing weak base groups.

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