A MODEL TO DESCRIBE THE ADSORPTION AND REDUCTION OF Cr (VI) FROM AN AQUEOUS SOLUTION BY AGAVE LECHUGUILLA BIOMASS

UN MODELO PARA DESCRIBIR LA ADSORCIÓN Y REDUCCIÓN DE Cr (VI) DE UNA SOLUCIÓN ACUOSA POR BIOMASA DE AGAVE LECHUGUILLA


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Abstract

The biosorption and reduction of Cr (VI) onto packed columns of Agave lechuguilla were analyzed using an advection-dispersion with a first order reaction (ADR) model and its analytical solution. Design parameters, such as an axial dispersion coefficient, a retardation factor, a distribution coefficient, and a general first-order decay constant, were estimated as functions of inlet metal ion concentration, pH, operation time, flow rate, cross-sectional column area, the density and length of the bed. The RMSE values (0.096, 0.170 and 0.180) with the corresponding flow rates of 1, 2, 3 (10⁻³) dm³ min⁻¹, respectively, indicated that the ADR model applied to the experimental data adequately explains the adsorption and reduction of Cr (VI) by lechuguilla biomass. The experimental results at different pH values along with the calculated parameters suggest that the adsorption of Cr (VI) took place in the internal pores and the reduction reaction occurred in the external surface of the biomass.

Keywords: ADR model, model; chromium (VI); adsorption; reduction; Agave lechuguilla.

Resumen

La biosorción y reducción de Cr (VI) en columnas empaquetadas con biomasa de Agave lechuguilla fueron analizadas usando un modelo de advección-dispersión con una reacción de primer orden (ADR) y su solución analítica. Parámetros de diseño, tales como un coeficiente de dispersión global, un factor de retardación, un coeficiente de distribución y un coeficiente de reacción de primer orden fueron estimados como función de la concentración del metal en el influente, del pH, del tiempo de operación, de la velocidad de flujo, de la área transversal de la columna, de la densidad y altura de la biomasa. Los valores de RMSE de 0.096, 0.170 y 0.180 correspondieron a las velocidades de flujo de 1, 2, 3 (10⁻³) dm³ min⁻¹, respectivamente, indicaron que el modelo ADR aplicado a los datos experimentales explican adecuadamente la adsorción y reducción de Cr (VI) por la biomasa de lechuguilla. Los resultados experimentales a diferentes valores de pH junto con los parámetros calculados sugieren que la adsorción de Cr (VI) toma lugar en los poros internos y la reacción de reducción ocurre en la superficie externa de la biomasa.

Palabras clave: modelo ADR, modelo, cromo (VI); adsorción; reducción; Agave lechuguilla.

1. Introduction

Chromium is one of the most toxic metals affecting the environment. Hexavalent chromium [Cr(VI)] is introduced into natural waters through several industrial processes including those of the textile, leather tanning, electroplating, metal finishing, and mining industries (Kotaś and Stasicka, 2000). Cr(VI) is considered a toxic material because of its tendency to oxidize other chemical species and because of its adverse impact on the lungs, liver, nervous system, and kidneys (World Health Organization, 1998). Gaballah and Kilbertus (1998) have found that conventional methods of removing Cr(VI) ions from waste water include electrochemical treatment, chemical reduction/neutralization/precipitation, ion exchange, carbon adsorption, membrane...
filtration, and electro and evaporative recovery; however, such processes have proven extremely expensive and ineffective. Biosorption, on the other hand, is a process that utilizes inexpensive dead biomass to sequester heavy metal contaminants from aqueous effluents. This emerging technology also attempts to overcome selectivity, a disadvantage of traditional decontamination processes. Natural materials from industrial, agricultural, or natural sources may potentially serve as inexpensive bioadsorbents. Volesky (2001) has published that the biosorption process offers advantages such as a high efficiency rate, low operating cost, and minimization of the volume of disposed chemical and/or biological sludge. Bailey et al. (1999) have shown that due to the health hazards of chromium, numerous studies concerning its removal from aqueous solutions have been performed using different biomasses. However, these studies have not analyzed the effect of the reduction of Cr(VI) to Cr(III) over the adsorption process. In addition, few studies have considered the adsorption and reduction of Cr(VI) by the same biomass (Daneshvar et al., 2002, Gardea-Torresdey et al., 2000, Kratochvil et al., 1998). Due to this fact, the simultaneous adsorption of the toxic Cr(VI) and its reduction to the less toxic Cr(III) as a method for the detoxification of wastewater effluents is an important field to study.

_Agave lechuguilla_, commonly known as lechuguilla, is one of the most common plants of the Chihuahuan Desert as well as other desert areas around Mexico and the U.S. However, it thrives in the hot and dry climate in southern states of Mexico, such as Guanajuato and Hidalgo. Peasants and small farmers use lechuguilla for several purposes such as syrup and alcoholic beverage production, and goods fabrication from the fibers. Additionally, roots and leaves contain active chemicals such as saponins and steroids, which are used in medicinal applications and as metal chelating agents (Gentry, 1982). During such processes high quantities of waste that remain rich in cellulose are produced. These characteristics make lechuguilla an excellent source of biomaterial for the removal of heavy metals from water and wastewater.

The possibility of using Agave lechiguilla biomass to remove heavy metals or other contaminants from wastewater represents an important social and economic advancement for desert and poor regions in countries such as Mexico.

The development and application of predictive and simulative mathematical models for the design of biosorption processes represents an important area in environmental engineering. These phenomenological models can economize time and effort when designing process systems for water and wastewater treatment. The determination of model parameters and verification of model validity can be accomplished by well-designed laboratory-scale experiments. The treatment process can be subsequently scaled to proportion using these parameters. The purpose of mathematical modeling is to reduce the scope and magnitude of pilot-scale studies and to design full-scale processes that are both economical and efficient. This manuscript describes the development and application of an analytical method for modeling Cr(VI) adsorption-reduction by lechuguilla biomass in packed column systems. In addition, the model assumptions and development of equations with appropriate initial and boundary conditions are discussed herein.

2. Materials and methods

Several non-living lechuguilla plants were collected near the city of Guanajuato, Gto., Mex. The plants were washed thoroughly using tap water in order to remove soil or debris. Only the leaves of the plants were utilized in this study, since they represent more than 90% of lechuguilla
plants. The washed samples were oven dried at 80 °C for 3 days and ground to pass through a 0.150 mm sieve using a Wiley mill. A stock solution of 4 mg dm\(^{-3}\) of Cr(VI) was prepared by using potassium dichromate (K\(_2\)Cr\(_2\)O\(_7\)) and deionized water. This concentration was calculated based on previous batch capacity studies. Previous studies also found the optimal pH for Cr(VI) biosorption by lechuguilla to be 2.0. It was also previously determined that the pH of point of zero charge—(pH)\(_{\text{pzc}}\)—or the pH at which the concentration of active sites in the surface of the biomass for the adsorption of Cr(VI) and Cr(III) on lechuguilla is identical (Chvedov et al., 2001)—was found to be 2.6. These conditions were set in the respective column studies. The pH of influent solution and biomass was adjusted using diluted solutions of HCl and NaOH. Column experiments were performed in glass columns of 0.07 dm of internal diameter. The biomass was packed to a bulk density (mass of adsorbent in a specific volume) of 6.52 (10 \(^5\) mg dm\(^{-3}\)) to get bed lengths of 0.5, 1 and 1.5 dm, respectively. The bed porosity, \(\varepsilon\), was determined as the volume of deionized water required to fill the porous of the dry bed (\(V_w\)) in the respective bed volume (\(V_b\)), \(\varepsilon = V_w / V_b\), dm\(^3\) dm\(^{-3}\) (Fig.1).

![Diagram of laboratory set-up for column studies](image)

Fig. 1. Schematic diagram of the laboratory set-up for column studies.

Column experiments were performed in triplicate at room temperature (22 °C). The Cr solution was fed to the top of the column by using a Masterflex pump (Cole-Parmer Model 7524). The effluents, from flow rates of 1, 2, and 3 (10 \(^{-3}\) ) dm\(^3\) min\(^{-1}\), were collected at time intervals of 6, 3 and 2 min, respectively, using a fraction collector Spectra/Chrom CF-1. An inductively coupled plasma optical emission spectrophotometer (Perkin Elmer Optima 4300 DV ICP-OES) was used to determine the Cr(Total) (Cr(VI) plus Cr(III)) in column influents and effluents. The ICP/OES was set at an emission line of 283.563 nm, detection limit of 0.007 mg dm\(^{-3}\) and the radio frequency of 1450 Hz. To determined the reduction of Cr(VI) to Cr(III) by the biomass, the Cr(VI) concentrations in the effluents were obtained spectrophotometrically by acid reaction with 1,5-diphenylcarbazide. The colored complex of Cr(VI) was read at 540 nm using a spectrophotometer (Spectronic 20UV, Milton Roy Co.). The difference between the concentrations of Cr (Total) and Cr(VI) was considered as the Cr(III) content in the effluent.
3. Model assumption and development

The mass balance on the adsorbate in an adsorption column with chemical reaction is expressed as follows (Hamed, 2002):

\[
\frac{\partial c}{\partial t} = \frac{U_o}{\varepsilon} \frac{\partial c}{\partial z} + D \frac{\partial^2 c}{\partial z^2} + \frac{\rho_{ads}(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} + r_n
\]  \hspace{1cm} (1)

In many models such as the proposed by Bohart and Adams (1920), Clark (1987), and Zhang and Cheng (2000) (adsorptive reactor model), which were originally utilized for the gas-charcoal adsorption system, the dispersion was considered negligible, thus, in these models the Eq. (1) is simplified as follows:

\[
\frac{\partial c}{\partial t} = -\frac{U_o}{\varepsilon} \frac{\partial c}{\partial z} - \frac{\rho_{ads}(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} + r_n
\]  \hspace{1cm} (2)

In addition, many studies related to Cr(VI) bioadsorption consider Cr(VI) as non-reactive species, which means that the net rate of reaction \(r_n = 0\) (Lehmann et al., 2001; Sağ and Aktay, 2001). Thus, the researchers simplified Eq. (2) as follows:

\[
\frac{\partial c}{\partial t} = -\frac{U_o}{\varepsilon} \frac{\partial c}{\partial z} - \frac{\rho_{ads}(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t}
\]  \hspace{1cm} (3)

These models frequently fail to offer satisfactory depiction of the effect of the adsorption process on solute transport. Some researchers, Johnson and Kapner (1990), van Zee et al. (1995), have demonstrated that the determination of an overall dispersion coefficient, \(D\), makes the model applicable for cases in which the transfer resistances are present in the liquid and solid phases. For these reasons, in the present study, the effect of the dispersion and the net reaction rate for chemical transport and simultaneous adsorption were considered as main parts of the development of the model. In redox reactions, adsorption is often a key step in reactions leading to precipitation or dissolution of solids and in biodegradation reactions. The effect of such reactions on the overall behavior can be evaluated by modifying the mass balance equation to consider the surface reaction. Assuming that these reactions are first-order decay with respect to the adsorbate’s dissolved concentration, and that in the liquid phase might be a zero-order production, the reaction rate expressions can be expressed as follows:

\[
r_i = -\mu c
\]  \hspace{1cm} (4)

\[
r_0 = \gamma
\]  \hspace{1cm} (5)

where \(\mu\) is the first order decay constant and \(\gamma\) is zero-order liquid phase source. Therefore the Eq. (1) can be written as follows:

\[
\frac{\partial c}{\partial t} = -\frac{U_o}{\varepsilon} \frac{\partial c}{\partial z} + D \frac{\partial^2 c}{\partial z^2} + \frac{\rho_{ads}(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} - \mu c + \gamma
\]  \hspace{1cm} (6)

The equilibrium distribution between the solid phase and the fluid phase can be described by a linear isotherm of the form:

\[
q = K_d c
\]  \hspace{1cm} (7)

and the partial derivative \(\frac{\partial q}{\partial t}\) can be substituted by the distribution coefficient \(K_d\) and the partial derivative \(\frac{\partial c}{\partial t}\).

Then,

\[
\frac{\partial q}{\partial t} = K_d \frac{\partial c}{\partial t}
\]  \hspace{1cm} (8)

And substituting Eq. (8) in Eq. (6), we obtained the following expression:

\[
\left(1 + \frac{\rho_{ads}(1-\varepsilon)}{\varepsilon} K_d\right) \frac{\partial c}{\partial t} = -\frac{U_o}{\varepsilon} \frac{\partial c}{\partial z} + D \frac{\partial^2 c}{\partial z^2} - \mu c + \gamma
\]  \hspace{1cm} (9)

\[
\left(1 + \frac{\rho_{ads}(1-\varepsilon)}{\varepsilon} K_d\right) \frac{\partial c}{\partial t} = -\frac{U_o}{\varepsilon} \frac{\partial c}{\partial z} + D \frac{\partial^2 c}{\partial z^2} - \mu c + \gamma
\]  \hspace{1cm} (10)
Then, the general advective-dispersion-reaction equation can be written as follows:

$$D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - R \frac{\partial c}{\partial t} = \mu c - \gamma$$  \hspace{1cm} (11)

where the retardation factor, $R$, is defined by:

$$R = \left(1 + \frac{\rho_{atm}(1 - \varepsilon)}{\varepsilon} K_d\right)$$  \hspace{1cm} (12)

and the pore velocity, $\nu$, is defined by:

$$\nu = \frac{U_0}{\varepsilon}$$  \hspace{1cm} (13)

To find the most descriptive alternative with a minimum of operation variables for a successful theoretical treatment of experimental data and simulation of bioadsorption breakthrough curves, several analytical solutions of the advection-dispersion equation, with first order reaction were analyzed (Ataie-Ashtiani et al., 1999; Hossain, 1999; Serrano, 2001). After the analyses, the van Genuchten analytical solution (van Genuchten, 1981), was modified and applied to the model. The equations, conditions, and variables used were the followings:

Eq. (11) was solved using the following initial and boundary conditions:

$$c(z,0) = C_i$$  \hspace{1cm} (14)

$$\left\{ \begin{array}{ll}
- D \frac{\partial c}{\partial z} + \nu c = \nu C_0 & 0 < t \leq t_0 \\
0 & t > t_0
\end{array} \right.$$

$$\left( - \frac{\partial c}{\partial z} \right)_{z=\infty} = 0$$  \hspace{1cm} (15)

where $C_i$ and $C_0$ are constants. The modified van Genuchten analytical solution using Laplace transforms (van Genuchten, 1981), is:

$$c(z,t) = \left\{ \begin{array}{ll}
(C_0 - \gamma / \mu) A(z,t) + B(z,t) & 0 < t \leq t_0 \\
(C_0 - \gamma / \mu) A(z,t) + B(z,t) - C_0 A(z,t - t_0) & t > t_0
\end{array} \right.$$  \hspace{1cm} (17)

where

$$A(z,t) = \frac{(\nu) \text{erfc} \left( \frac{zR - ut}{\sqrt{4Drt}} \right) \exp \left( \frac{(\nu - u)z}{2D} \right)}{(\nu + u)} + \frac{(\nu) \text{erfc} \left( \frac{zR + ut}{\sqrt{4Drt}} \right) \exp \left( \frac{(\nu + u)z}{2D} \right)}{(\nu - u)}$$

$$+ \frac{(\nu^2) \text{erfc} \left( \frac{zR + ut}{\sqrt{4Drt}} \right) \exp \left( \frac{zu}{D - R} \right)}{2\mu D}$$  \hspace{1cm} (18)

$$B(z,t) = \left( \frac{\gamma}{\mu} - C_i \right) \left[ \text{erfc} \left( \frac{zR - ut}{\sqrt{4Drt}} \right) \frac{\nu^2 t}{D} + 1 \right] \text{erfc} \left( \frac{zR + ut}{\sqrt{4Drt}} \right)$$

$$\times \exp \left( - \frac{ut}{R} \right) + \frac{\gamma}{\mu} \left( C_i - \frac{\gamma}{\mu} \right) \exp \left( - \frac{tu}{R} \right)$$

$$+ \exp \left( - \frac{(zR - ut)^2}{4Drt} \right) \sqrt{\frac{\nu^2 t}{\pi DR}}$$  \hspace{1cm} (19)
and

\[ u = \sqrt{\frac{4uD}{\nu^2} + 1} \]  \tag{20}  

The root-mean-square-error (RMSE) between the experimental and predicted values is defined by:

\[ \text{RMSE} = \sqrt{\frac{\sum (C_i^{\text{experimental}} - C_i^{\text{predicted}})^2}{N}} \]  \tag{21}  

where \( N \) is the total number of data points.

The variables required and applied in the model to describe the system included the following:

- Operating condition such as \( C_0 \), input metal ion concentration (mg dm\(^{-3}\)); \( t \), time (min); \( Q \), flow rate (dm\(^{-3}\) min\(^{-1}\)).
- Biosorbent physical properties such as \( \rho_{ads} \), density (mg dm\(^{-3}\)).
- Column packing characteristics such as internal diameter (dm), \( A \), cross-sectional area (dm\(^2\)); \( \varepsilon \), porosity; \( z \), bed length column (dm); \( v \), pore water velocity, \( v = \frac{Q}{AE} \) (dm min\(^{-1}\)).

This model generates the following design and scale up parameters:

- \( D \), axial dispersion coefficient (dm\(^{2}\) min\(^{-1}\));
- \( R \), retardation factor;
- \( K_d \), distribution coefficient (dm\(^3\) mg\(^{-1}\));
- \( \mu \), general first-order decay constant (min\(^{-1}\));

4. Results and discussion

The breakthrough curves for Cr(Total), Cr(VI) and Cr(III) in the column effluent at 1.5 dm bed length, \( 10^{-3} \) dm\(^{3}\) min\(^{-1}\) flow rate, and pH values of 2 and 2.6 are shown in Fig. 2 and 3, respectively. Fig. 3 shows that after 1 h, the reduction (Cr(III)) was approximately 20 %, at 250 min, 35%, and at 330 min, it dropped down to 18 % of the total Cr in the effluent. The lessening of Cr(VI) reduction with time suggests that reaction sites in the column were used up/exhausted during the experiment. The reduction reaction is described by the following equation:

\[ HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \]  \tag{22}  

Fig. 2. Breakthrough curves for chromium species in the column effluent at 1.5 dm bed length, \( 10^{-3} \) dm\(^{3}\) min\(^{-1}\) flow rate, 4 mg dm\(^{-3}\) inlet metal ion concentration and pH 2.
Fig. 3. Breakthrough curves for chromium species in the column effluent at 1.5 dm bed length, $10^{-3}$ dm$^3$ min$^{-1}$ flow rate, 4 mg dm$^{-3}$ inlet metal ion concentration and pH 2.6.

Table 1. Operational conditions of the column experiments.

<table>
<thead>
<tr>
<th>Metal in influent</th>
<th>Cr(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input concentration, $C_0$</td>
<td>4.0 mg dm$^{-3}$</td>
</tr>
<tr>
<td>Flow rates, $Q$</td>
<td>$1, 2, 3 \times 10^{-3}$ dm$^3$ min$^{-1}$</td>
</tr>
<tr>
<td>Lechuguilla particles density, $\rho_{ads}$</td>
<td>$8.7 \times 10^5$ mg dm$^{-3}$</td>
</tr>
<tr>
<td>Column internal diameter</td>
<td>0.07 dm</td>
</tr>
<tr>
<td>Bed porosity, $\varepsilon$</td>
<td>0.25</td>
</tr>
<tr>
<td>Bed high column, $z$</td>
<td>0.5, 1, 1.5 dm</td>
</tr>
<tr>
<td>pH</td>
<td>pH 2 and (pH)$_{pzc}$ 2.6</td>
</tr>
</tbody>
</table>

Table 2. Model parameters corresponding to experimental conditions for Cr(VI) adsorption by lechuguilla biomass.

<table>
<thead>
<tr>
<th>pH $\times 10^{-3}$ dm$^3$ min$^{-1}$</th>
<th>$Q$ $\times 10^{-3}$ dm$^3$ min$^{-1}$</th>
<th>$D$ (dm$^2$ min$^{-1}$)</th>
<th>Retardation</th>
<th>$K_d$ $\times 10^6$ dm$^3$ mg$^{-1}$</th>
<th>$\mu$ (min$^{-1}$)</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>0.77</td>
<td>21.92</td>
<td>8</td>
<td>1.11</td>
<td>0.096</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.76</td>
<td>15.75</td>
<td>5.6</td>
<td>0.60</td>
<td>0.170</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.66</td>
<td>9.68</td>
<td>3.3</td>
<td>0.47</td>
<td>0.180</td>
</tr>
<tr>
<td>2.6</td>
<td>1</td>
<td>0.72</td>
<td>19.23</td>
<td>6.9</td>
<td>1.17</td>
<td>0.115</td>
</tr>
<tr>
<td>2.6</td>
<td>2</td>
<td>0.77</td>
<td>14.24</td>
<td>4.9</td>
<td>0.61</td>
<td>0.117</td>
</tr>
<tr>
<td>2.6</td>
<td>3</td>
<td>0.62</td>
<td>9.56</td>
<td>3.2</td>
<td>0.49</td>
<td>0.193</td>
</tr>
</tbody>
</table>
The adsorption of Cr(VI) at pH 2.6, which is the pH of point of zero charge for lechuguilla biomass, was lower than the one observed at pH 2. This trend in pH dependence suggests that the Cr binding by lechuguilla takes place through ionic exchange mechanism. Selomulya et al. (1999) demonstrated that Cr(VI) exists in solution predominantly as HCrO$_4^-$ at low pH values and as CrO$_4^{2-}$ at high pH values. Other studies have shown that Cr(III) tends to form cationic hydroxides in solutions such as Cr(OH)$_2^+$, Cr(OH)$_3^+$, and Cr$_2$(OH)$_4^{2+}$.

Column parameters ($D$, $R$, and $\mu$) for the model given by van Genuchten’s analytical solution (Eqs. 17-20) were estimated from the Cr(VI) column biosorption data by using the Mathematica 4.1 computer program (Wolfram Research, Inc.) to minimize the RMSE during early time periods prior to the decline in reaction rate. Table 1 summarizes the operational conditions used in these column experiments. To cover the initial time period of the column, the simulated breakthrough curves were plotted using the data previous to the breakthrough point. In this time period, the Cr(VI) reduction reaction is approximately first order. An example of the lumped breakthrough simulated curves at pH 2 and a $10^{-3}$ dm$^3$ min$^{-1}$ flow rate are given in Fig. 4.

![Lumped breakthrough curves of Cr(VI) sorption by lechuguilla biomass.](image)

**Fig. 4.** Lumped breakthrough curves of Cr(VI) sorption by lechuguilla biomass. The model profiles are presented with different lines and the points denote experimental values for bed lengths of (—) 0.5, (---) 1, and (- - -) 1.5 dm; flow rate, $10^{-3}$ dm$^3$ min$^{-1}$; pH 2, and $C_o$, 4 mg dm$^{-3}$.

The parameters generated by the ADR model are compiled in Table 2. This table shows that an increase in flow rate decreases the distribution coefficient without a significant change of the reaction constant ($\mu$), which represents the reduction of Cr(VI) to Cr(III). As seen in Table 2, at pH 2 and $1 \times 10^{-3}$ dm$^3$ min$^{-1}$ flow rate, $\mu$ was 1.11 min$^{-1}$, while at $3 \times 10^{-3}$ dm$^3$ min$^{-1}$ flow rate, it was 0.47 min$^{-1}$. Similar results were found when the pH was 2.6. This suggests that Cr(VI) adsorption takes place in internal pores of the biomass into which Cr(VI) diffuses slowly. These results also suggest that the reduction reaction took place in the external surface of the lechuguilla. Similar results were reported by Sharma and Forster (1995) for sphagnum peat moss.

The distribution coefficient on other hand, decreased as pH increased. This
supports the idea that the adsorption of Cr(VI) anions is expected to decrease as pH increases. Therefore, the pH dependence of Cr(VI) binding observed in this study was consistent with the proposed ion exchange mechanism. In addition, the RMSE values, which varied from 0.096 to 0.193 (see Table 2), indicate that the ADR model applied to experimental data fairly explains the adsorption and reduction of Cr(VI) by lechuguilla, during early time periods before the reaction sites became depleted. The column reduction capacities of lechuguilla were estimated from the differences between the areas generated by the model assuming $\mu = 0$ (no reduction reaction) and the respective experimental values when $\mu > 0$ (reduction reaction), ($A_R$), for each set of experiments. The reduction capacities were calculated using the following equation:

$$C_R = \frac{A_R Q}{W}$$  (23)

where $C_R$ is the bed reduction capacity (mg g$^{-1}$), $A_R$ is the reduction area (mg min dm$^{-1}$), $Q$ is the flow rate (dm$^3$ min$^{-1}$), and $W$ (g) is the mass of adsorbent at the respective bed length, $z$ (dm).

Fig. 5 shows an example of this process. As seen in this figure, the reduction capacity of Cr(VI) to Cr(III), which is directly proportional to $A_R$, increased as the length of the column increased. For example, at a 10$^{-3}$ dm$^3$ min$^{-1}$ flow rate and bed length of 0.5 dm, the reduction capacity was 56.3 mg/g, while at a bed length of 1.5 dm it was 95.1 mg g$^{-1}$. In addition, the adsorption capacities for Cr(VI) were calculated from the experimental breakthrough curves. Using the same bed length as for the reduction capacity, we calculated the adsorption capacity. At a bed length of 0.5 dm the adsorption capacity was 55.6 mg g$^{-1}$. While at the bed length of 1.5 dm it was 124 mg g$^{-1}$. The residence times $\tau$ (min) were calculated using the Eq. (24):

$$\tau = \frac{V}{Q} = \frac{Az}{Q} = \frac{z}{U_o}$$  (24)

where, $V$ is the column bed volume (dm$^3$), $A$ is the cross-sectional area (dm$^2$), $z$ is bed high column (dm), $Q$ is the flow rate of the influent (dm$^3$ min$^{-1}$) and $U_o$ is the average approach velocity of the metal aqueous solution (dm min$^{-1}$), respectively. The residence times were determined at the same operational conditions used to calculate the adsorption and reduction capacities. Fig. 6 shows the relationship between bed reduction, adsorption capacities and the residence times at pH 2, which was the optimal for the adsorption and reduction reaction of Cr(VI) by lechuguilla. At low residence times, low reduction capacity occurred, which was higher than the adsorption capacity. However, at high residence times the adsorption capacity increased while the reduction capacity decreased. As seen in Fig. 6, at a residence time of 1 min the adsorption and reduction capacities were 42.8 and 49.11 mg g$^{-1}$, respectively. However, at a residence time of 6 min these adsorption and reduction capacities were 135.7 and 99.1 mg g$^{-1}$ respectively. According to the authors’ knowledge, there are no bibliographical references about this relationship. The values of correlation coefficients ($R^2$) for the bed adsorption and reduction capacity related to $\tau$ were 0.9802 and 0.9716, respectively. These values suggest that the adsorption and reduction capacities depend proportionally on the metal solution residence time, and then the relationships showed in the figure can be used to design a packed column with appropriate cross-sectional area and length.

The average reduction and adsorption capacities for lechuguilla packed columns were equal to 66.8 mg g$^{-1}$ and 80.5 mg g$^{-1}$, respectively, which are similar or higher than values reported for other biomass packed columns. For example, Sharma and Foster (1995) reported that sphagnum peat moss has
a reduction capacity of 65.9 mg g⁻¹ and an average adsorption capacity of 64.3 mg g⁻¹. The same authors, Sharma and Forster (1996), reported that activated carbon has a Cr(VI) reduction capacity of 63.5 mg g⁻¹ and adsorption capacity of 75.5 mg g⁻¹, and that the reductive capacity of leaf mould is 4.81 mg g⁻¹ and its adsorptive capacity is 25.9 mg g⁻¹.

The experimental values and the calculated parameters found in this research demonstrated that the ADR model and its analytical solutions are effective tools for modeling the advective and dispersive transport of the adsorption and reduction of Cr(VI) from an aqueous solution by *Agave lechuguilla* biomass.

The lumped breakthrough curves of Cr(VI) sorption by lechuguilla biomass for theoretical data (µ = 0) and experimental values (µ > 0). The model profiles are represented by different lines and the points denote experimental values for bed lengths of ( ) 0.5, (---) 1, and ( - ) 1.5 dm; flow rate, 10⁻³ dm min⁻¹; pH 2, and C₀, 4 mg dm⁻³.

The chromium(VI) bed reduction and adsorption capacities of lechuguilla biomass at different residence times. The set of experiments were performed at pH 2.
Conclusions

The results of this investigation showed that lechuguilla biomass had a Cr(VI) reduction and adsorption capacities of 66.8 mg g\(^{-1}\) and 80.5 mg g\(^{-1}\), respectively. The experimental data and calculated parameters using the ADR model suggest that Cr(VI) is reduced to Cr(III) in the external surface of the biomass. The ADR model may be applied to other reactive solutes using different biomasses. The analytical solution of the proposed model can also be applied to simulate the breakthrough curves to determine the scaleup parameters of packed columns, using all variables that constitute the equation of the ADR.

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