Equilibrium and Thermodynamic Studies on Adsorption of Trivalent Chromium by Sericin-Alginate Particles Prepared from Bombyx Mori Cocoons

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Particles prepared from the blend between sericin and alginate were used as biosorbent of Cr(III) ions from aqueous solution. In order to show how is the Cr(III) distribution between the liquid phase and the solid phase at the equilibrium, biosorption isotherms were obtained at four different temperatures (20, 30, 40, 60 °C). The isotherm models of Langmuir, Freundlich and Dubinin–Radushkevich were used to test the equilibrium biosorption data. Better fittings were obtained for both Langmuir and Dubinin–Radushkevich models. Additionally, the thermodynamic parameters enthalpy change, entropy change, and Gibbs free energy change were calculated and the biosorption process was found to be exothermic and spontaneous. The results shown that sericin-alginate particles are a promising biosorbent material for the efficient removal of Cr(III).

1. Introduction

Sericin constitutes from 20 to 30 % of the total mass of the silkworm Bombyx mori (B. mori) cocoons. It is a macromolecular and hydrophilic protein with molecular weight ranging from about 10 to 300 kDa. Sericin has to be removed during silk processing and is mostly discarded in wastewater. It is estimated that the processing of 400,000 t of dry cocoons produces about 50,000 t of sericin (Zhang, 2002). Recently, the use of sericin as alternative biosorbent of metal contaminants has been evaluated. For instance, Chen et al. (2011) investigated the selective removal of gold employing sericin powder as biosorbent and obtained biosorption capacity of 1 mmol/g. Nevertheless, the weak structural properties and high solubility in water of sericin, added to its gelatinous nature and wide range of molecular weight, causes this protein to form fragile 2D and 3D structures that limit its application as biosorbent. The blending with other polymers can enhance these inferior biophysical properties and it is possible thanks to the polar side chain of sericin, made of hydroxyl, carboxyl and amino groups (Dash et al., 2009). The trapping of biosorbents in calcium alginate beads is one of the most favourable alternatives (Sillerová et al., 2015). Alginate is a natural polymer composed of 1,4'-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues. The sodium salt of alginate is most frequently linked in both aqueous and alcoholic solutions of CaCl2. The "egg-box" model explains that the 3D network is formed due to the interaction of the divalent cation (Ca2+) with the blocks of M and G residues (Sillerová et al., 2015). Recently, da Silva et al. (2014) investigated the production of particles from the blend between sericin and alginate, ionic cross-linked in both aqueous and alcoholic solutions of CaCl2 and thermal cross-linked. Da Silva et al. (2015) evaluated the application of those particles as biosorbent of Cu(II) and Zn(II) ions and the obtained percentages of reduction of those metals concentrations were up to 75 % and 65 %. The present work aims to study the biosorption of trivalent chromium ions [Cr(III)] from aqueous solution on sericin-alginate particles. The interest in the removal of Cr(III) lies in the fact that, although it is an essential element to human metabolism, long-term exposures can cause cancer and skin allergic reactions (Yun et al., 2001). The drinking water guideline from the World Health Organization (WHO) for total chromium is of...
0.05 mg/L (WHO, 2011). In this study, Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were used to evaluate the Cr(III) equilibrium biosorption data and thermodynamic parameters were determined.

2. Experimental procedures

2.1 Materials

_B. mori_ cocoons were supplied by Bratac Silk Mills Company (Brazil). All the reagents used were of analytical grade. Sodium alginate was purchased from Sigma–Aldrich (United Kingdom). The aqueous solution of Cr(III) was produced by dissolving Cr(NO$_3$)$_3$·9H$_2$O (Neon, Brazil) in ultrapure water (Milli-Q Millipore System). The solution pH was varied using HNO$_3$ solution.

2.2 Biosorbent preparation

Sericin-alginate particles (S-A particles) were produced based on the methodology from da Silva et al. (2015). Firstly, _B. mori_ cocoons were manually cleaned and cut into pieces of about 1 cm$^2$. The pieces were washed with tap water, triple rinsed with deionized water and dried at 50 °C in continuous flow oven. In the proportion of 40 g of cocoons for 1 L of deionized water, sericin was extracted in autoclave (Phoenix Luterco, AV-18) at 120 °C (1 kgf/cm$^2$) for 40 min. The sericin solution was separated from the silk fibres using paper filter and was stored in sealed container, maintained at least for 12 h at room temperature. High molecular sericin was obtained by freezing/thawing method and had its concentration adjusted to 25 g/L by dilution. With Ultra Turrax (IKA, T18), sodium alginate was incorporated to the sericin solution in the proportion of 20 g/L and the formed blend was dripped in CaCl$_2$ aqueous solution (30 g/L) for the production of the S-A particles. The cross-linking process was completed by continuous agitation of the particles in CaCl$_2$ solution at 60 rpm for 12 h in Jar Test (Milan JT-203). Finally, the particles were washed with deionized water, dried at 50 °C and submitted to thermal cross-linking at 100 °C for 24 h in continuous flow oven.

2.3 Biosorption experiments

Isotherm studies were carried out in a temperature-controlled shaker (Jeio Tech, SI-600R) with agitation speed fixed at 200 rpm and at different temperatures (20, 30, 40 and 60 °C). A series of 125 mL Erlenmeyers flasks were filled with 0.4 g of biosorbent and 40 mL of Cr(III) solutions having initial concentrations ranging from 0.02 to 8.5 mmol/L and initial pH adjusted to 3.5. In order to prevent chromium precipitation, which may occur above pH 5.5 (Tan et al., 2015), one drop of HNO$_3$ was added hourly to each flask throughout the experiments. Preliminary tests indicated that 4 h contact time was sufficient to reach the biosorption equilibrium of Cr(III) on S-A particles. Therefore, in the equilibrium tests it was adopted the contact time of 6 h, after that, samples were taken and centrifuged for 10 min at 4,000 rpm (Centurion Scientific, C2041). The equilibrium concentrations of Cr(III) were determined by atomic absorption spectroscopy (Shimadzu, AA-7000) and the equilibrium biosorption capacities, $q_e$ (mmol/g), were calculated using the Eq(1):

$$q_e = \frac{(C_0 - C_e)V}{m}$$

(1)

where, $C_0$ and $C_e$ (mmol/L) are the initial and equilibrium concentration, respectively; $V$ is the solution volume (0.04 L); and $m$ is the mass of S-A particles (0.4 g).

3. Results and discussion

3.1 Effect of temperature

The influence of temperature on the biosorption of Cr(III) onto S-A particles is shown in Figure 1, which presents the experimental results for the range of lower initial concentrations. It can be observed that for very low Cr(III) initial concentrations, the biosorption capacity remains almost constant for all temperatures. However, at higher concentrations, the equilibrium biosorption capacity increases with increases in temperature. The favouring in biosorption capacity may be related to the chemical interaction between the S-A particles and Cr(III) ions, increased kinetic energy of Cr(III) or the availability of more active sites at higher temperatures (Karthikeyan et al., 2005). Similarly, Li et al. (2004), employing wine processing waste sludge, obtained higher Cr(III) biosorption capacities with increasing in temperature from 20 to 50 °C. Sandy et al. (2012) also verified that the higher the temperature the better the removal of copper ions by organo-bentonite.

3.2 Biosorption isotherms

The analysis of equilibrium data provides relevant design data for biosorption systems. In this study, the relationship between biosorbed Cr(III) ions ($q_e$) and metal ions remaining in solution ($C_e$) at given temperature has been described by the two-parameter isotherm models of Langmuir, Freundlich and Dubinin-Radushkevich (D-R). The experimental and predicted isotherms are shown in Figure 2.
Figure 1: Effect of temperature on the biosorption of Cr(III) onto S-A particles

Figure 2: Biosorption isotherms of Cr(III) onto S-A particles at temperatures of: (a) 20 and 30 °C, (b) 40 and 60 °C

Non-linear regression analysis of the isotherm models was carried out in Statistica 7.0 software and the estimated constants are presented in Table 1, in conjunction with the correlation coefficient, \( R^2 \), and mean absolute percentage deviation, \( D \), calculated by Eq(2):

\[
D = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{q_{exp} - q_{pred}}{q_{exp}} \right| \times 100
\]  

where, \( N \) is the number of equilibrium data points, \( q_{exp} \) and \( q_{pred} \) (mmol/g) are the experimental and predicted amount of Cr(III) biosorbed at the equilibrium.

Table 1: Isotherm constants for biosorption of Cr(III) onto S-A particles at different temperatures

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Temperature (°C)</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
<td>( q_{max} ) (mmol/g)</td>
<td>0.0087</td>
<td>0.0234</td>
<td>0.1015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_L ) (L/mmol)</td>
<td>49.7731</td>
<td>26.3156</td>
<td>7.1194</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R^2 ) (-)</td>
<td>0.0314</td>
<td>0.0595</td>
<td>0.0162</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R^2 ) (-)</td>
<td>0.9042</td>
<td>0.9359</td>
<td>0.9824</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( D ) (%)</td>
<td>16.21</td>
<td>23.11</td>
<td>34.34</td>
</tr>
</tbody>
</table>
The magnitude of $E$ is used to estimate the type of biosorption mechanism. If the value of $E$ lies between 8 and 16 kJ/mol, the biosorption can be related to ion exchange; meanwhile, if the value is less than 8 kJ/mol, the biosorption occurs physically (Ngah and Fatinathan, 2010). Since the calculated values of $E$ for all the studied temperatures are lower than 8 kJ/mol, the predominant biosorption mechanism is physical (Table 1). The comparison of $R^2$ and $D$ values indicates that both Langmuir and D-R isotherm models fit well the biosorption experimental data. Therefore, the surface of S-A particles is composed of homogeneous and heterogeneous patches and the Cr(III) biosorption is rather complex, involving more than one mechanism. The
broad range of Cr(III) initial concentrations investigated in the present study can be associated to the poor fitting of Freundlich model, since it is known to be satisfactory for low concentrations (Baccar et al., 2010).

3.3 Comparison of S-A particles with other biosorbents
The maximum sorption capacity $q_{\text{max}}$ from Langmuir equation is useful in the evaluation of Cr(III) uptake capacity of different sorbents. In Table 2, values of $q_{\text{max}}$ from S-A particles were compared with other alternative sorbents reported in literature. Despite the varying experimental conditions of each study, S-A particles presents reasonable $q_{\text{max}}$ and can be considered a viable biosorbent for the removal of Cr(III) ions.

Table 2: Comparison of maximum biosorption capacity of Cr(III) by alternative sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Experimental conditions</th>
<th>$q_{\text{max}}$ (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue of alginate extraction from</td>
<td>pH 3, 20 °C</td>
<td>0.635</td>
<td>Bertagnoli et al. (2014)</td>
</tr>
<tr>
<td>Sargassum filipendula</td>
<td>pH 3, 30 °C</td>
<td>0.611</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 5, 30 °C</td>
<td>0.0837</td>
<td>Gupta and Ali (2004)</td>
</tr>
<tr>
<td>Bagasse fly ash</td>
<td>pH 5, 40 °C</td>
<td>0.0827</td>
<td></td>
</tr>
<tr>
<td>Vineyard pruning waste</td>
<td>pH 4.2, 30 °C</td>
<td>0.2395</td>
<td>Karaoglu et al. (2010)</td>
</tr>
<tr>
<td>Cork powder</td>
<td>Natural pH, 22 °C</td>
<td>0.1212</td>
<td>Machado et al. (2002)</td>
</tr>
<tr>
<td>Expanded perlite</td>
<td>pH 3.6, 20 °C</td>
<td>0.011</td>
<td>Chakir et al. (2002)</td>
</tr>
<tr>
<td>Sericin-alginate particles</td>
<td>pH 3.5, 30 °C</td>
<td>0.0234</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>pH 3.5, 40 °C</td>
<td>0.1015</td>
<td></td>
</tr>
</tbody>
</table>

3.4 Estimation of thermodynamic parameters
Due to the dependence on temperature, the Langmuir constant $K_L$ was applied to estimate the changes in standard Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$), using Eq(8) and Eq(9). As the $K_L$ value at 40 °C was much lower than the others found, it was neglected in this thermodynamic study.

\[
\Delta G^\circ = -RT \ln K_L \tag{8}
\]

\[
\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}
\]

where, $R$ is the universal gas constant (8.314 J/mol/K) and $T$ is the absolute temperature (K). The values of $\Delta H^\circ$ and $\Delta S^\circ$ can be determined from the slope and intercept, respectively, of the plot of $\ln K_L$ versus $1/T$.

The values of the thermodynamic parameters are listed in Table 3. The obtained $\Delta G^\circ$ negative values are associated with the spontaneous nature of the biosorption of Cr(III) onto the S-A particles, while the positive $\Delta S^\circ$ value indicates an increasing in the randomness at the solid/solution interface during the process. The negative value of $\Delta H^\circ$ suggests that the biosorption process is exothermic. Nevertheless, from the equilibrium experimental data the opposite was expected, since the biosorption capacity increases with increasing temperature. Bertagnoli et al. (2014) also observed experimentally the favourability of Cr(III) biosorption onto residue of alginate extraction from Sargassum filipendula at higher temperatures, but obtained a negative value of $\Delta H^\circ$ in the thermodynamic study. As the thermodynamic parameters are calculated based on traditional sorption models, e.g. Langmuir, parametric inconstancies can arise from a lack of thermodynamic consistency in the assumptions of the model subject to various experimental conditions (Xiaofu, 2009).

Table 3: Thermodynamic parameters for the biosorption of Cr(III) onto S-A particles at different temperatures

<table>
<thead>
<tr>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol/K)</th>
<th>20 °C</th>
<th>30 °C</th>
<th>40 °C</th>
<th>60 °C</th>
</tr>
</thead>
</table>

4. Conclusions
Sericin, a waste product from the silk industry, was converted into S-A particles and used as biosorbent for the removal of Cr(III) from aqueous solution. Equilibrium studies demonstrated increases in biosorption capacity with increase in temperature. Both Langmuir and D-R isotherm model provides good correlation of experimental equilibrium data, indicating that the biosorption of Cr(III) onto S-A particles involves more than one mechanism. The maximum biosorption capacities based on Langmuir model were 0.0234 and 0.1015 mmol/g at 30 and 40 °C, respectively. These results are comparable with maximum sorption capacities of other alternative sorbents reported on the literature. The thermodynamic study indicates the spontaneous and exothermic nature of the biosorption process. Concluding, this work shows that S-A particles may be used as alternative biosorbent for the removal of Cr(III).
Acknowledgments
The authors thank Bratac Silk Mills Company for the silkworm cocoons granted and CAPES, CNPq (Proc. 470615/2013-3) and FAPESP (Proc. 2011/51824-8 and Proc. 2015/13505-9) for the financial support.

References