Removal of cadmium from water using by-product Crambe abyssinica Hochst seeds as biosorbent material

Fernanda Rubio, Affonso Celso Gonçalves Jr, Ana Paula Meneghel, Cesar Ricardo Teixeira Tarley, Daniel Schwantes and Gustavo Ferreira Coelho

ABSTRACT

The effectiveness of Crambe abyssinica Hochst seeds by-product as a biosorbent for the removal of cadmium ions from wastewater was analyzed. The biomass of crambe was characterized by scanning electron microscopy, infrared spectroscopy and determining the point of zero charge. The optimum adsorption conditions obtained were 400 mg of biomass in a solution of pH 6.0 and contact time of 60 min to remove 19.342 mg g\(^{-1}\) cadmium ions. The isotherms of adsorption were constructed and, according to the mathematical linearization, the best fitting followed the Freundlich and Dubinin–Radushkevich models, describing a multilayer adsorption and chemical interaction, also confirmed by the pseudo-second order model and enthalpy value. In the desorption process, about 79% of cadmium ions that had been adsorbed were recovered. The same conditions applied for studying the isotherms of adsorption and desorption were used for comparative study with activated carbon. It was concluded that the use of crambe by-product as biosorbent for cadmium removal in wastewaters was not only a viable alternative to activated carbon, but also required no previous treatment, so it represents a sustainable material with high applicability and low environmental impact.

Key words | biosorption, cadmium, crambe, sustainability, water remediation

INTRODUCTION

Crambe abyssinica Hochst belongs to the cruciferous family, and has attracted great interest due to the oil content in its seeds (36–38%), which is used in many applications such as lubricants, additives production, polymers, paints, coating bases, and biodiesel production. The oil extraction from crambe seeds produces a large amount of by-product, rich in proteins, but, due to its unpalatable characteristics and the presence of substances called glucosinolates, it cannot be used in animal feed (Wang et al. 2000; Pitol et al. 2010).

Lately, an alternative that has been much studied with agroindustrial by-products is its use on the removal of pollutants by adsorption. So, in many cases it has shown satisfactory results (Ibrahim et al. 2010). Different materials are used as adsorbents and activated carbon is one of the most used. Despite being very efficient, activated carbon is too expensive to be used in wastewater treatment on a larger scale (Debrassi et al. 2011).

Thus, the demand for low-cost and new adsorbent materials has been increasing, principally the ones from renewable sources, which are easy to handle and have less environmental impact. These materials have proved to be particularly efficient in dealing with wastewater problems (Pehlivan et al. 2008).

Cadmium is a heavy metal that is widely used in industrial areas such as batteries, alloys and electroplating, and it is considered very toxic. The exposure to cadmium negatively affects the kidneys, bone structure and respiratory system in humans; in addition it can be classified as a carcinogen (Bayramoglu & Arica 2011; Strumylaite et al. 2011).

Regarding the advantages attributed to the culture of crambe and the need for finding new natural adsorbents, this study aimed to examine the adsorption of the by-product of crambe seeds on biosorption of Cd present in contaminated waters.
MATERIAL AND METHODS

Preparation and characterization of the biosorbent

The crambe seeds were dried for 36 h at 60 °C in an oven. After that, the seeds were crushed and the oil was extracted with n-hexane by means of the Soxhlet system (IUPAC 1988) resulting in the by-product, which was dried at 70 °C for 24 h to evaporate the used solvent. The biosorbent was sieved (14 mesh – Bertel) aiming at standardizing the particles sizes.

A morphological characterization of the by-product of crambe seeds was obtained by SEM (scanning electron microscopy); the equipment used was the scanning electron microscope FEI Quanta 200, operating at 30 kV. The infrared (IR) spectrum was obtained by the technique of potassium bromide pellets in a Fourier transform IR spectrophotometer (Shimadzu FTIR-8300) with 4 cm⁻¹ resolution.

To characterize the load on the adsorbent’s surface, the point of zero charge (pHPZC) of the biosorbent was determined. The process involved adding 50 mg of biosorbent in 50 mL aqueous potassium chloride at 0.05–0.5 mol L⁻¹, with initial pH values ranging from 2.0 to 10.0. Solutions were stirred for 24 h at 200 rpm and 25 °C. At the end of this period the final pH values were obtained, thus resulting in a graph of the final pH variation as a function of the initial pH; the point that reached the zero value of pH variation corresponded to the pHPZC (Mimura et al. 2010).

Adsorption studies

Effect of the solution’s pH and amount of adsorbent mass

Cadmium was used in solutions of 10 mg L⁻¹, prepared from CdCl₂ salt using distilled and deionized water. The pH of the solutions was adjusted to 5.0, 6.0 and 7.0 using HCl and NaOH, both at 0.1 mol L⁻¹.

Cadmium ion solutions (50 mL) were added to the masses of biosorbent, ranging from 200 to 1,200 mg in 125 mL flasks. Samples were agitated at 200 rpm for 90 min at 25 °C. Thereafter 10 mL aliquots were removed and centrifuged at 3,000 rpm (629.77 gravity) for 5 min, for the later determination of Cd concentrations in solution by flame atomic absorption spectroscopy (Welz & Sperling 1999).

The Cd amount adsorbed was determined using Equation (1):

\[ Q_{eq} = \frac{(C_0 - C_{eq})}{m} V \]  

in which \( Q_{eq} \) is the amount of metal adsorbed by adsorbent mass (mg g⁻¹), \( C_0 \) and \( C_{eq} \) are the initial metal concentration and in the solution equilibrium (mg L⁻¹), respectively, \( V \) is the solution volume (mL), and \( m \) the by-product mass (g).

Effect of contact time

The optimal contact time needed for maximum cadmium removal was established. Systems containing the biosorbent and the Cd solution (10 mg L⁻¹) were stirred at 200 rpm and 25 °C at the time intervals: 20, 40, 60, 80, 100, 120, 140, 160 and 180 min.

Adsorption isotherms

The optimal experimental conditions were used for the construction of isotherms. Herein, 50 mL samples of aqueous solution of Cd metal at different initial concentrations (10–90 mg L⁻¹) at pH 6.0 were transferred to flasks containing 400 mg biosorbent. The system remained in agitation at 200 rpm and 25 °C for 60 min.

Desorption

The biosorbent material used in the adsorption isotherms was separated from the aqueous solutions using the filtration method, washed in distilled and deionized water and dried at 60 °C for 24 h. The biosorbent mass obtained was placed in contact with 50 mL of hydrochloric acid solution at 0.1 mol L⁻¹ and then stirred at 200 rpm for 60 min.

Thermodynamics of adsorption

The temperature influence on the adsorptive process was evaluated under 25, 35, 45, 55 and 65 °C, using the optimal conditions obtained in the previous studies and solution of 50 mg L⁻¹.

Comparative study with activated carbon

Using the same optimal conditions previously determined for the biosorbent, other studies were realized to compare the adsorption and desorption using powder activated carbon (analytical grade).
RESULTS AND DISCUSSION

Biosorbent characterization

Figure 1 shows the scanning electron micrograph for a biosorbent sample. In the image magnified up to 20,000 times, the irregular and heterogeneous nature of biomass can be seen, which favors the adherence of metal ions present in the aqueous solution.

Figure 2 shows the peaks obtained from the IR spectrum analysis of the by-product of crambe seeds sample. The strong band at 3,328 cm$^{-1}$ can be attributed to the vibration stretching of O–H, present in carbohydrates, proteins, fatty acids, cellulose, lignin units and absorbed water (Gonçalves Jr et al. 2010; Han et al. 2010). The thin band in the region of 2,925 cm$^{-1}$ suggests the stretching of C–H of alkane groups, and the peak at 1,647–1,429 cm$^{-1}$ suggests the stretching vibration of C–O of the amides and carboxylic groups; the band at 1,537 cm$^{-1}$, in addition to the vibration stretching of C–O, can also be attributed to the N–H stretching present in proteins. The band at 1,251 cm$^{-1}$ is associated with the C–O stretching, but in phenols, and the band at 1,053 cm$^{-1}$ is also linked to the C–O stretching, but suggests the presence of lignin (Han et al. 2010), which is well known for its metal adsorption capacity (Dermibas 2008).

The identification of functional groups in the biomass is important, because the biosorption is a result of electrostatic interactions and formation of complexes between the metal ions and functional groups present in the biosorbent (Dos Santos et al. 2010). From the IR spectrum analysis of the by-product of crambe seeds, it is suggested that this material has functional groups such as hydroxyl, amide, carbonyl and carboxyl groups, which enable the adsorption of heavy metals (Ngah & Hanafiah 2010).

The functional groups of the studied adsorbent in IR also contribute to the determination of the adsorbent surface charge (pH$_{PZC}$), thus allowing the identification of the pH at which the adsorbent surface has a neutral charge (Mimura et al. 2010).

The result of the pH$_{PZC}$ determination for by-product of crambe seeds was 5.5 (Figure 3), confirming the data obtained by Oliveira et al. (2009) who also performed the pH$_{PZC}$ test with the crambe by-product.
Adsorption study

Effect of solution pH and adsorbent mass

The study showed that solutions at pH 6.0 had higher percentage of Cd ion removal than at the other pH values (Figure 4), confirming that the pH_{PZC} was pH 5.5, showing that in this condition the biosorbent behaved as a negatively charged species. In the literature, pH 6.0 values have been reported in Cd adsorption (Farooq et al. 2011).

The influence of the biosorbent mass on the Cd adsorption (Figure 4) shows that, for masses higher than 400 mg, the percentage of adsorption was approximately constant due to the fact that a large number of sites in the biosorbent surface are available during the early stage, but after a time the remaining sites are difficult to occupy due to the formation of aggregates and repulsive forces between the ions in the solid and those free in solution (Farooq et al. 2011). Thus, according to the results, the biosorbent mass used in subsequent studies was 400 mg.

Effect of contact time

The Cd adsorption by the by-product of *Crambe abyssinica* reached equilibrium after 60 min of agitation (Figure 5).

The kinetics of adsorption of Cd on the by-product of crambe was investigated using four models. The pseudo-first order model (Equation (2)) describes that the adsorption rate is proportional to the number of sites unoccupied by the solutes (Witek-Krowiak et al. 2011).

\[
\log (Q_e - Q_t) = \log Q_e - \frac{K_1 t}{2.303}
\]  

in which \(Q_t\) is the amount adsorbed at time \(t\) (min) given in mg g\(^{-1}\), \(K_1\) is the speed constant for pseudo-first order (min\(^{-1}\)).

Unlike the pseudo-first order model (Equation (2)), the pseudo-second order model predicts an adsorption of chemical nature (Ho & Mckay 1999):

\[
\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e}
\]  

where \(K_2\) is the speed constant of pseudo-second order (g mg\(^{-1}\) min\(^{-1}\)).

The Elovich model (Equation (4)) describes the kinetics of chemisorption behaviors (Witek-Krowiak et al. 2011) and is often validated for systems in which the adsorbent surface is heterogeneous (Debrassi et al. 2011).

\[
Q_e = A + B \ln t
\]  

where \(A\) represents the initial speed of chemisorption and \(B\) is related to the extent of surface coverage and the chemisorption activation energy.

Another kinetic model widely used is the intraparticle diffusion (Equation (5)). This model assumes that the diffusion of the liquid film surrounding the adsorbent is negligible and the intraparticle diffusion is what controls the main steps of the adsorption process (Yang & Al-Duri 2005).

\[
Q_e = K_{id} t^{1/2} + C_i
\]
where $K_{id}$ is the intraparticle diffusion constant (g mg$^{-1}$ min$^{-1/2}$), and $C_i$ is a constant (mg g$^{-1}$) that suggests the thickness of the boundary layer effect.

Although the intraparticle diffusion model was shown to have a higher value for the coefficient of determination ($R^2$ 0.964) than the pseudo-first order (0.847) and Elovich models (0.874), the pseudo-second order model demonstrated a better fit by having $Q_{eq}$ experimental values (0.902) similar to the $Q_{eq}$ calculated (0.894) and the $R^2$ value (0.998) around 1.

The kinetic study in question reinforces the bibliographic study performed by Farooq et al. (2011), whose bioremediation of divalent metals on various adsorbents were best described by the pseudo-second order model, indicating that the speed mechanism control is based on a chemical adsorption (Ho & Mckay 1999).

**Adsorption isotherms**

To interpret the experimental data, four linearized isotherm models were employed. The Langmuir model (Equation (6)) suggests that the adsorption on a uniform surface composed of a finite number of sites assumes a monolayer adsorption (Witek-Krowiak et al. 2011).

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{q_m \times b} + \frac{C_{eq}}{q_m}$$

in which $q_m$ is related to the maximum capacity of adsorption and $b$ (or the Langmuir equilibrium constant $K_L$) is related to the adsorbent-adsorbate interaction forces.

Unlike the Langmuir model, the Freundlich model (Equation (7)) describes multilayer adsorption and it is applicable to heterogeneous surfaces (Witek-Krowiak et al. 2011).

$$\log Q_{eq} = \log K_F + \left(\frac{1}{n}\right) \times \log C_{eq}$$

in which $K_F$ is related to the adsorption capacity and $n$ to the intensity of adsorption and the adsorbent-adsorbate interaction.

The Dubinin–Radushkevich isotherm (D–R) (Equation (8)) is applied to determine the adsorption energy and distinguish if the process is physical or chemical (Farooq et al. 2011).

$$\ln Q_{eq} = \ln Q_d - B_d \times \varepsilon^2$$

in which $Q_d$ is the maximum capacity of adsorption (mol g$^{-1}$), $B_d$ expresses the adsorption energy (mol$^2$ J$^{-2}$), which is related to the average power of sorption ($E$) ($E = 1/\sqrt{2B_d}$). $\varepsilon$ is the Polanyi potential ($\varepsilon = RT \ln(1 + 1/C_{eq})$) in which $R$ is the universal gas constant (kJ mol$^{-1}$ K$^{-1}$) and $T$ is temperature (K).

The D–R and Freundlich models better described the adsorption process for both adsorbents as can be observed by the $R^2$ values (Table 1). This suggests that the adsorption is influenced by the adsorbent surface heterogeneity, with more than one type of active site interacting with the metal, which indicates that the adsorption occurred in multilayers (Montanher et al. 2005).

Related to the parameter $n$, both adsorbents showed adsorption intensity, the obtained $n$ value was greater than 1, representing a beneficial and favorable adsorption according to Witek-Krowiak et al. (2011).

The maximum capacity of adsorption calculated and estimated ($q_m$) for the by-product of crambe seeds was 19.342 mg g$^{-1}$: a satisfactory result, being superior to other biosorbents used in Cd removal, such as maize cob (Zea mays) (Igwe & Abia 2007), wheat straw (Triticum aestivum) (Farooq et al. 2011), and rice husk (Kumar & Bandyopadhyay 2006). The $q_m$ value for activated carbon was higher than that for the by-product of crambe, but it is worth noting that the biosorbent derived from crambe had not undergone any previous treatment, unlike coal which needs many processing steps to be effective.

### Table 1 | Parameters of the mathematical models of Langmuir, Freundlich and Dubinin–Radushkevich for by-product of C. abyssinica seeds and activated carbon in Cd adsorption

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Adsorbents</th>
<th>C. abyssinica</th>
<th>Activated carbon</th>
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<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m$ (mg g$^{-1}$)</td>
<td>19.342</td>
<td>21.258</td>
<td></td>
</tr>
<tr>
<td>b or $K_L$ (L mg$^{-1}$)</td>
<td>0.028</td>
<td>0.094</td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.958</td>
<td>0.936</td>
<td></td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_F$ (L g$^{-1}$)</td>
<td>0.582</td>
<td>2.137</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>1.178</td>
<td>1.418</td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.991</td>
<td>0.969</td>
<td></td>
</tr>
<tr>
<td><strong>Dubinin–Radushkevich</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_d$ (mol g$^{-1}$)</td>
<td>$4.7 \times 10^{-4}$</td>
<td>$5.6 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>$E$ (kJ mol$^{-1}$)</td>
<td>8.143</td>
<td>9.685</td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.984</td>
<td>0.968</td>
<td></td>
</tr>
</tbody>
</table>
Regarding the variation in free energy ($E$) of the D–R model, which is the energy involved in the transfer of 1 mol of solute from the solution to the adsorbent surface, Farooq et al. (2011) and Fávere et al. (2010) state that, if the adsorption process is physical, the average energy is 1–8 kJ mol$^{-1}$, but, if the process has a chemical nature, the $E$ value will be greater than 8 kJ mol$^{-1}$. It can be observed (Table 1) that the $E$ values were greater than 8 kJ mol$^{-1}$, which confirms that both adsorbents have a chemical interaction with the metal. Also, the values of $b$, which represents the interaction power, were higher in the carbon (0.094 mg L$^{-1}$) than the biosorbent (0.028 mg L$^{-1}$), which confirms the superior results of the $E$ value for the commercial adsorbent.

**Desorption**

The Cd ion adsorption on the by-product of crambe seeds was 76%, and from this adsorbed amount approximately 79% of the ions were recovered in the desorption. The activated carbon had 91% of adsorption, being capable of desorbing 67% of this value. These differences in adsorption and desorption between the two adsorbents can be explained by the active carbon having greater interaction ($b$) and adsorption intensity ($n$) (Table 1) with the metal under consideration.

These percentage values of desorption can be considered satisfactory for a possible reuse of the adsorbent material for new stages of adsorption (Dos Santos et al. 2010).

**Thermodynamics of adsorption**

To determine the thermodynamic parameters including enthalpy ($\Delta H$), entropy ($\Delta S$) and Gibbs free energy ($\Delta G$), Equations (9) and (10) were used:

$$
\Delta G = -RT \times \ln K_d \tag{9}
$$

$$
\ln(K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}
$$

where $K_d$ is the equilibrium constant at temperature $T$ ($Q_{eq}/C_{eq}$), $R$ is the universal gas constant, $T$ is temperature (K).

The $\Delta S$ value found (62.734 J mol$^{-1}$ K$^{-1}$) confirmed that the process has greater randomness in the system and the decrease in $\Delta G$ values of 4.017–1.507 kJ mol$^{-1}$ suggests that the reaction is favored by high temperature (Farooq et al. 2011).

The amount of cadmium adsorbed increased from 3.772 to 5.046 mg g$^{-1}$, also increasing with temperature, indicative of an endothermic process, which is supported by the positive $\Delta H$ value of 22.711 kJ mol$^{-1}$. Moreover, according to Uncun et al. (2008) and Gundogdu et al. (2009), enthalpy values exceeding 20 kJ mol$^{-1}$ indicate a chemisorption process for the adsorption of cadmium ions onto crambe biosorbent. This result is also supported by the pseudo-second order kinetic model fitting and the free energy, $E$, (8 kJ mol$^{-1}$) calculated from the D–R adsorption isotherm.

**CONCLUSION**

The characterization of the by-product showed a favorable structure for adsorption. In this study, the better adsorption of Cd ions was found in solutions with pH 6.0, confirming the pH dependence on the adsorption process for the value found of 5.5 in the determination of pH$\text{PZC}$. The Freundlich and D–R models better described the adsorption data. The interaction of the by-product with the metal ions pointed to a chemisorption due to the best kinetics fit by the pseudo-second order model, the value of the average energy of sorption ($E$) of D–R greater than 8 kJ mol$^{-1}$ and the value of 22.711 kJ mol$^{-1}$ for the enthalpy variation. The percentage of metal recovery was 79%, indicating possible biosorbent reuse.

This study demonstrated that the by-product of crambe seeds, which did not undergo any previous treatment, can be used as a potential Cd adsorbent and be an effective tool in the remediation of environmental compartments contaminated by toxic heavy metals.

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