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Biosorption of Copper(II) onto Sericin Powder Derived from Cocoons of the Silkworm *Bombyx Mori*: Kinetics, Equilibrium and Thermodynamics Studies

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The aim of this study was to evaluate the biosorption of copper(II) ions onto sericin powder derived from *Bombyx mori* silkworm cocoons. Sericin powder, obtained from aqueous extraction (at 120 °C and 20 min extraction) and cold denaturation, was used as biosorbent to remove ions copper from wastewater. Batch adsorption system was used to investigate the kinetic mechanism, equilibrium and thermodynamic of copper(II) biosorption. The kinetics and equilibrium were studied at pH 4.8 at different temperatures (from 20 to 60 °C). The Langmuir, Freundlich and Temkin isotherm models were used for the equilibrium modelling and the kinetics were evaluated by the fitting of convective mass transfer and diffusion models. The maximum sericin uptake of copper(II) was 21.77 ± 0.21 mg g^{-1}, at 20°C. The kinetic and equilibrium studies showed fast adsorption and interaction limited to the monolayer surface, with pseudo-second order and Langmuir model providing the best fits. Thermodynamic studies indicated that the system is spontaneous, exothermic and that chemical interactions govern the adsorption process. The results revealed that sericin powder has the potential to be used as a biosorbent for the treatment of wastewater containing the ions copper(II).

1. Introduction

Many industrial processes in the plating industry involve heavy metals for metal finishing and their effluent must be treated prior to discharge. Copper ions, in particular, are one of the most abundant heavy metal ions in the wastewater of several industries. Excessive intake of copper ions by humans results in its accumulation in the liver and causes gastrointestinal problems. For this reason, it is essential to remove these ions from wastewater with a cost effective treatment (Kurniawan et al., 2006; Ozicemin and Mericboy, 2010).

As alternative technology, biosorption has received increasing interest owing to its cost effectiveness, ability to produce less sludge and environmental friendliness, and thus a practical bioprocess for ion metal or dye-containing wastewater needs to be developed (Srinivasan and Viraraghavan, 2010). Biosorption is the process of binding contaminants on the surface of biological material by the chemical affinity of pollutant with the functional groups of biosorbent, as the carboxyl, hydroxyl,amino, carbonyl, phosphate, and sulfonic groups (Podstawczyk et al., 2015). Some studies with biosorbent, as biomass (Gupta et al., 2006; Hu et al., 2015) and proteins (Chen et al. 2012, Nazari et al., 2014) showed potential to remove copper from wastewater.

In this context, sericin (water-soluble protein derived from silkworm cocoons) showed high potential to use in development of wastewater treatment (Silva et al., 2015). Sericin is a globular protein, with molecular weight ranging from 10 to 310 kDa, comprising 18 amino acids, most of which have strong polar side groups. Sericin is especially rich in aspartic acid and serine, which represent around 19 % and 32 % of the sericin molar amino acid composition, respectively (Wu et al., 2007). In general, sericin is discharged in silk manufacturing wastewater during the silk degumming step (Capar et al., 2008). The recovered sericin, with its natural structure, can be applied in the development of many types of biofilms and structural materials (Zhang, 2002; Altman et al., 2003). Many studies showed the development of biomaterials applied in membrane separation and adsorption processes (Gimenes et al., 2007;Turbiani et al., 2011,Chen et al., 2012; Silva et al., 2015).

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In this context, we focus on the study of the adsorption of copper ions present in aqueous solution onto silk sericin powder derived from the degumming of the cocoons of *Bombyx mori* silkworms. With this aim, adsorption batch experiments were performed to investigate the thermodynamics, equilibrium and adsorption kinetics of copper ions onto sericin adsorbent.

2. Materials and Methods

2.1 Biosorbent

Sericin powder was obtained from degumming of silkworm cocoons, according to the methodology described by Silva et al. (2012). The degumming process was conducted by hot water extraction, with cocoons of *Bombyx mori* obtained from the northwest region of Paraná State, Brazil. Almost 12.5 grams of chopped cocoon were placed within 250 mL of deionized water in an Erlenmeyer for thermal degumming process in an autoclave (Phoenix, model AV – 30) at 120 °C for 20 min. The degummed solution was frozen at -20 °C, and submitted to lyophilisation for 24 hours in a compact system (Liotop^{TM}, model L101), to change the sericin tertiary structure and turn it insoluble in water. The dried material was ground (Marconi^{TM} mill, model MA630/1) for 5 min at 150 rpm to obtain sericin in powder, with an average size larger than 100 μm.

Aqueous solution of ions copper were prepared by dissolving $Cu(SO_4).5H_2O$ in de-ionized water. The pH solution was 4.8, in which copper is predominantly in its form of copper(II) ions. The concentrations of copper(II) in solutions, before and after the biosorption, were determined by spectrophotometry with cuprizone colorimetric method (Labdin and Taylor; 1998). The colored complex Cu^{2+} with cuprizone solution was read at 600 nm (spectrophotometer Femto^{TM}, model 600 plus).All reagents used were of AR grade.

2.2 Adsorption studies

The biosorption experiments were carried out in a temperature-controlled orbital shaker (Tecnal^{TM} TE-421) at a constant speed (150 rpm). For each assay, 50 mL of copper(II) solution with determined amount of Copper(II), at pH 4.8,was placed into a 125 mL conical flask with 50 ± 0.5 mg of sericin powder, and the flasks were hermetically sealed. After the adsorption assay, the samples were filtered through quantitative filter papers (J. Prolab®, nominal pore size of 40 μm) and the supernatant were submitted to ion copper concentration analysis.

The uptake of Copper(II) at time $\underline{t}$, i.e. $\underline{q}$ (mg g^{-1}), was obtained through the mass balance, according to eq. (1), where $\underline{V}$ (mL) is the solution volume, $\underline{Co}$ and $\underline{C}$ (mg L^{-1}) are the initial concentration and the liquid-phase concentration of copper(II), respectively, and $\underline{w}$ (g) is the mass of sericin powder.

$$q = \frac{[Co - C] \cdot V}{w} \tag{1}$$

2.3 Kinetic models

The experimental kinetic data was modelled with the convective mass transfer models of Lagergren pseudo-first-order (eq. 2) and pseudo-second-order (eq. 3) (Ho and Mckay, 1998). These models assume that the adsorption mechanism is similar to the surface chemical reaction process, where $\underline{q(t)}$ and $\underline{q_{EQ}}$ are the amount of copper(II) adsorbed onto sericin at time $\underline{t}$ and at equilibrium, respectively, and $\underline{K_1}$ and $\underline{K_2}$ are the kinetic constants of the pseudo-first order and pseudo-second order models, respectively

$$\frac{dq(t)}{dt} = K_1 \cdot \left(q_{EQ} - q(t)\right) \tag{2}$$

$$\frac{dq(t)}{dt} = K_2 \cdot \left(q_{EQ} - q(t)\right)^2 \tag{3}$$

The diffusion models of Weber-Morris (eq. 4) and Crank (eq. 5) were also evaluated in this study. As reported in Qiu et al. (2009), these models consider that the restrictive adsorption mechanism involves the diffusion of the liquid film surrounding the solid surface through the internal pores of the adsorbent, where K_W and K_D are the diffusion constants of the Weber-Morris and Crank models, respectively.

$$q(t) = K_W \cdot \sqrt{t} \tag{4}$$

$$q(t) = q_{EQ} \cdot \left\{1 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp(-n^2 \cdot K_D \cdot t)\right\} \tag{5}$$

2.4 Adsorption equilibrium

The adsorption equilibrium was evaluated using Langmuir, Freundlich and Temkin isotherms The Langmuir isotherm is a non-linear model which assumes the monolayer uptake of the solute on a homogeneous surface, with uniform adsorption energy for all binding sites and with no interaction between the adsorbed molecules (Ruthven, 1984). The model is given by eq. (6), where q_{EQ} (mg g^{-1}) is the amount adsorbed at equilibrium, C_{EQ} is the equilibrium concentration of the copper(II) (mg L^{-1}), K_L is Langmuir equilibrium constant (L mg^{-1}) and q_M is the maximum adsorption capacity of the adsorbent (mg g^{-1}).

$$q_{EQ} = \frac{q_M \cdot K_L \cdot C_{EQ}}{1 + K_L \cdot C_{EQ}} \tag{6}$$

Freundlich and Temkin isotherms consider that the sorption takes place on a heterogeneous adsorbent surface and multilayer adsorption process, expressed by eq. (7) and (8), respectively, where K_F is the Freundlich constant, n is the heterogeneity factor, K_T (L g^{-1}) is the Temkin constant, R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the adsorption temperature and B is related to the heat of adsorption.

$$q_{EQ} = K_F \cdot C_{EQ}^{\frac{1}{n}} \tag{7}$$

$$q_{EQ} = \frac{R \cdot T}{B} \cdot \ln\left(K_T \cdot C_{EQ}\right) \tag{8}$$

The thermodynamic parameters of the adsorption were determined from equilibrium constants (K_{EQ}), i.e., the constants corresponding to the distribution of the solute between the solid and liquid phases at equilibrium for each temperature. Equilibrium constants, for each temperature, were calculated according to the method of Khan and Singh (1988). The standard Gibbs free energy (ΔG_{ADS}) of adsorption was calculated according to eq. (9). The slope and intercept of the Van't Hoff equation, along with the corresponding plots of $\ln(K_{EQ})$ versus T^{-1} (eq. 10) were used to determinate the enthalpy (ΔH_{ADS}) and entropy (ΔS_{ADS}) of adsorption:

$$\Delta G_{ADS} = -R \cdot T \cdot \ln K_{EQ} \tag{9}$$

$$\ln K_{EQ} = \frac{\Delta S_{ADS}}{R} - \frac{AH_{ADS}}{R \cdot T} \tag{10}$$

2.5 Validating the kinetic and isotherm models

The parameters of the kinetic and isotherm models were obtained by non-linear least squares regression analysis. The Levenberg–Marquardt algorithm was employed as the interactive method and the StatSoft^{TM} STATISTICA software (version 7.0) was used for all calculations. The coefficient of determination (R^2) and sum of the squares of residues (SSR) were obtained to determine the validity of the models.

3. Results and Discussion

3.1 Adsorption Kinetics

The kinetics of the adsorption of copper ions onto sericin was assessed from curves of the adsorption capacity as a function of time at pH 4.8, obtained for different temperatures, using an initial concentration of copper ions of 50 mg L^{-1}. In Table 1, the models parameters are reported together with the correspondent coefficients of determination (R^2) and sum of the squares of residues (SSR) for each model evaluated, while the Figure 1 showed the fitting of models with the experimental data.

As related by Silva et al. (2015), sericin powder obtained of the *Bombyx mori* cocoons by hot water degumming process shows isoionic point between pH 3.2 and 3.5. This means that the sericin surface charge is negative for pH solutions above pH of 3.5, and at pH 4.8 the predominant ionic form of copper is the divalent (Cu^{++}), so, the adsorption process tends to be favourable. The amino acid composition of sericin has a large amount of hydroxyl and carboxyl groups, notably due the presence of serin, aspartic acid and arginine, with almost 21.56 %, 14.00 % and 11.95 % of the total amino acid composition of the sericin powder, respectively (Silva et al 2015). This high amount of polar amino acids suggests the potential of sericin to be used as the biosorbent for wastewater treatment (Chen et al., 2012).

Table 1: Kinetic parameters fitted to experimental data

Kinetic Models	Parameters	20°C	40°C	60°C
Pseudo-first-order	K_1(min^{-1})	20.39 ± 0.00	23.42 ± 0.00	23.02 ± 0.00
	q_{EQ}(mg g^{-1})	20.39 ± 0.32	19.29 ± 0.12	17.78 ± 0.12
	SSR	3.071	0.424	0.440
	R² (%)	99.15	99.87	99.84
Pseudo-second-order	K_2(g mg^{-1} min^{-1})	1.402 ± 0.504	1.020 ± 0.374	1.485 ± 0.558
	q_{EQ}(mg g^{-1})	21.00 ± 2.12	19.47 ± 9.08	17.96 ± 8.64
	SSR	0.026	0.045	0.051
	R² (%)	99.98	99.95	99.94
Intraparticle diffusion Weber–Morris	K_W(min^{-1})	2.84 ± 0.70	2.66 ± 0.68	2.45 ± 0.63
	SSR	672.464	632.275	535.652
	R² (%)	32.29	28.51	28.71
Intraparticle diffusion Crank	K_C(min$^{-0.5}$)	30.90 ± 0.00	30.31 ± 0.00	29.70 ± 0.00
	q_{EQ}(mg g^{-1})	20.30 ± 0.69	19.20 ± 0.59	17.70 ± 0.54
	SSR	14.221	10.401	8.914
	R² (%)	99.15	99.87	99.84

As shown in Figure 1, independently of the temperature applied, the adsorption of the copper(II) onto the sericin powder was a fast process, with a high amount of copper adsorbing within the first 5 min of contact.

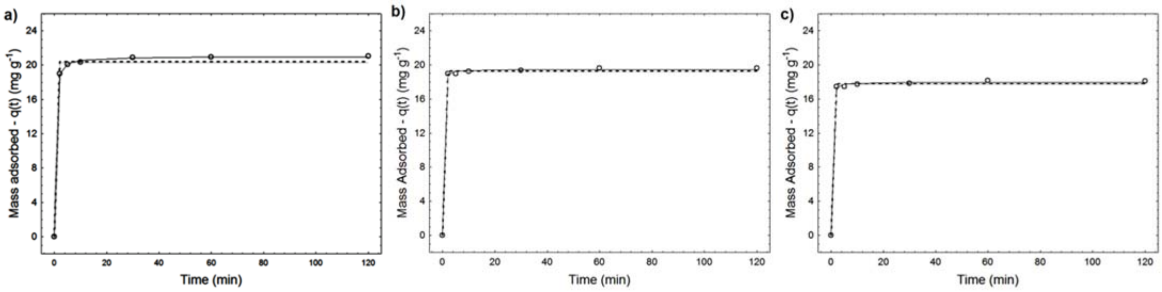

Figure 1: Kinetics of copper(II) adsorption by silk sericin.(a) T= 20˚C, (b)T= 30˚C, (c)T= 40˚C experimental data (○), pseudo-first-order (- - -), pseudo-second-order (—),and Crank model ( ).

It was observed that the pseudo-second order model provided a best fit, with highest values of R² values (99.94 - 99.98 %) and the lowest values of SSR (0.068 – 0.158). The pseudo-second order model assumes that the adsorption occurs due to the difference between the concentrations at the adsorbate surface and in solution, and mass transfer is limited only by external resistance. As reported by Silva et al. (2015), the sericin powder morphology (obtained by hot water degumming and cold denaturation) is nonporous material with surface area around 20 m². Due to the specific morphology and its amino acid composition, the interaction between sericin and copper(II) is specific (the functional groups of the sericin, as hydroxyl and carboxyl, with a large amount of pairs of electrons available to interact with copper(II) by complex link)and superficial, i.e., the predominant mechanism is the convective mass transfer, as well described by pseudo-second-order.

The Weber-Morris model provided low R² values, between 28.51 and 32.69 %. This indicates that internal mass transfer is not a relevant resistance mechanism. The Crank model approaches the convective mass transfer models, but this model showed high SSR, due it does not describe the initial transient adsorption.

3.2 Adsorption equilibrium

Figure 2 shows the relationship between the amount of copper(II) adsorbed per gram of sericin powder (q_{EQ}) and the equilibrium concentration (C_{EQ}) in liquid phase. The maximum copper(II) adsorption was 21.77 ± 0.21 mg g^{-1} at 20°C. As showed in Figure 2, the results show that the amount of adsorbed solute decreased with an increase in temperature, indicating that the adsorption process was exothermic. Similar results was obtained by Khormaei et al (2007), with a maximum uptake of copper(II) onto sour orange residue of 21.70 mg g^{-1} at 20°C and pH 5.0.

The isotherm parameters and statistical analysis are summarized in Table 2. The Langmuir isotherm shows the best fit for all temperatures evaluated, with R² ranging from 93.47 to 99.48 % and lowest values of SSR, except to equilibrium study at 40 °C. The monolayer adsorption process, characteristic of the Langmuir isotherm, is compatible with adsorption process that involves chemical adsorption, as the complex link between metals like copper(II) and hydroxyl and carboxyl groups presents in the amino acids, what indicated preferential link between sericin surface and ion in a single monolayer.

Table 2: Langmuir, Freundlich, and Tenkim parameters fitted to experimental data

Isotherm Models	Parameters	20°C	40°C	60°C
Langmuir	q_{MAX}(mg g^{-1})	23.03 ± 3.12	21.38 ± 8.35	19.89 ± 1.17
	K_L (L mg^{-1})	0.18 ± 0.02	0.16 ± 0.05	0.19 ± 0.01
	SSR	0.522	3.789	0.051
	R² (%)	99.48	93.74	99.66
Freundlich	K_F (L^n mg^{1-n} g^{-1})	10.41 ± 0.61	9.13 ± 1.00	9.98 ± 1.02
	n	0.17 ± 0.02	0.19 ± 0.03	0.15 ± 0.03
	SSR	0.740	2.314	1.314
	R² (%)	94.96	86.85	90.68
Temkin	K_T(L mg^{-1})	736.80 ± 46.06	817.96 ± 129.24	1086.93 ± 166.55
	B	0.18 ± 0.02	0.16 ± 0.05	22.54± 22.73
	SSR	0.44	2.38	0.97
	R² (%)	96.20	88.48	93.42

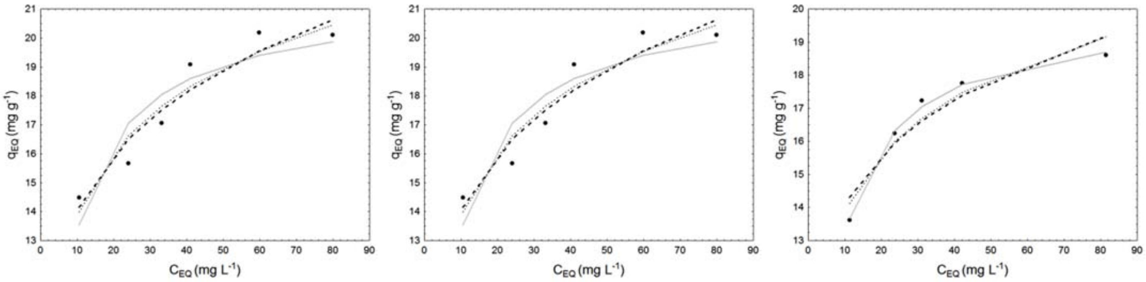

Figure 2: Copper(II) adsorption equilibrium: experimental data (●) obtained at 20 °C (a), 30 °C (b) and 40 °C (c), and Langmuir (—), Freundlich (- - -) and Temkin (…..) isotherms.

Table 3 reports the equilibrium thermodynamics parameters, that is, the adsorption equilibrium constant for the copper(II) adsorption onto sericin (K_{EQ}), Gibbs free energy (ΔG_{ADS}) and the enthalpy (ΔH_{ADS}) and entropy (ΔS_{ADS}) of adsorption. The ΔG_{ADS} values were negative for all temperatures investigated thus, indicating that the adsorption process is spontaneous, while the ΔH_{ADS} of -27.80KJ mol^{-1} shows that the process is exothermal. Moreover, the obtained ΔH_{ADS} value of -27.80 KJ $mol^{-1}$is and the same order those for chemisorption process (Ruthven, 1984), what suggests that the adsorption of copper(II) onto the sericin powder is governed by chemical interaction mechanisms in which some functional groups of the amino acids complex the ion copper available onto the aqueous phase.

Table 3: Equilibrium constants, standard Gibbs free energy and enthalpy and entropy of adsorption of copper(II) onto sericin powder.

Temperature (°C)	K_{EQ}	ΔG_{ADS} (KJ mol^{-1})	ΔH_{ADS} (KJ mol^{-1})	ΔS_{ADS} (J mol^{-1} K^{-1})	R² (%)
20	13.287	-6.31	-27.08	-70.48	98.46
40	7.527	-5.26			
60	3.497	-3.45			

The ΔS_{ADS} value of -70.48 J mol^{-1} K^{-1}suggests that the surface of sericin changed from a disordered state to a more organized conformation. This behaviour is compatible with the chemical process by metal complex onto functional groups, which the copper(II) forms complex bonds with electrophilic groups (as hydroxyl and carboxyl), changing the stereochemical conformation of the surface, reducing the mobility of the amino acid protein in secondary and tertiary protein structure.

4. Conclusions

The results of this study revealed that sericin powder has good potential for the treatment of aqueous solutions containing copper(II) ions. The maximum adsorption capacity obtained at equilibrium was 21.77 ± 0.24mg g^{-1}at 20°C. An increase in the temperature reduced the adsorption capacity of the sericin. The kinetic and equilibrium study showed fast biosorption and monolayer interaction, with the pseudo-second-order and Langmuir isotherm model providing the best fits. In accordance with thermodynamics analysis, the adsorption of copper(II) ions onto sericin is an exothermic process which involves complex chemical links of copper(II) ions to the strong polar chains of sericin (hydroxyl and carboxyl groups).

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