CHEMICAL ENGINEERING TRANSACTIONS

VOL. 56, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim

ISBN 978-88-95608-47-1; **ISSN** 2283-9216

DOI: 10.3303/CET1756316

Equilibrium Study of Cadmium Ions Adsorption on Sericin/Alginate Particles

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Cadmium is a pollutant widely found in industrial effluents and its toxicity affects the ecosystem and presents human health risk. The adsorption can be used to remove toxic metals in dilute solutions. Industrial waste, such as sericin, can efficiently replace conventional bioadsorbent materials. Sericin is a protein present in silkworm cocoon and is usually discarded in effluent of spinning processes. Alginate is a polysaccharide used to improve the characteristics of the blend. The objective of this study was to investigate the use of sericin/alginate particles as bioadsorbent to remove cadmium ions (Cd^{2+}) in waste water through adsorption equilibrium study. Equilibrium experiments were conducted to evaluate the influence of adsorption temperature (10 °C, 20 °C, 40 °C and 60 °C), which indicated that the cadmium adsorption capacity increased with decreasing temperature. Adsorption isotherm models, Langmuir, Freundlich, Dubinin-Radushkevich and Temkin were used to analyse the equilibrium data. Cadmium adsorption equilibrium could be described by the Freundlich adsorption model at all the temperatures essayed. The values of the n parameter, which are greater than unity, indicate that Cd^{2+} ions are favourably adsorbed by sericin/alginate particles at the temperature range studied.

1. Introduction

Environmental pollution due to the technological development is a critical issue, mainly in respect to toxic metals, potential pollutants widely found in industrial effluents. Among the toxic metal, cadmium has been classified as a human carcinogen and teratogenic. It has been released into the environment through electroplating and manufacturing of batteries and pigments (Boparai et al., 2011).

Conventional methods for the removal of toxic metal ions from waste water include chemical reduction, co-precipitation, coagulation, complexation, electrochemical treatment and adsorption. Adsorption is considered very attractive considering its pollutant removal efficiency in dilute solutions. This technique generally involves the use of conventional adsorbents, such as activated carbon, which are effective in removing various pollutants. However, they are generally expensive and have a high cost of regeneration, thereby motivating the research for new low cost materials.

Bioadsorption is based on the binding capacity of various metals with organic materials, including wastes of industrial operations, as in the case of sericin, disposed in the processing of silk.

The sericin, a protein that constitutes 20 - 30 % of the total mass of cocoons of the *Bombyx mori*, has amino acids with strong polar groups such as hydroxyl, carboxyl and amino groups. These groups allow crosslinking, copolymerisation and formation of blends with other polymers such as alginate. This allows achieving better material characteristics, since the sericin has poor structural properties and high solubility in water (Zhang, 2002). Alginate is a polysaccharide easy to obtain, available from natural sources, renewable and abundant. It can be found in brown algae and bacteria and is biodegradable and have good biocompatibility (Volesky, 1990). Recently, Silva et al. (2015) studied the production of sericin/alginate particles by ionic and thermal reticulation processes. The potential of these particles as bioadsorbent of toxic metals was evaluated and the authors obtained concentration reductions of about 75 % and 65 % for copper and zinc ions, respectively.

Please cite this article as: Lima J.O., Ragassi M.F., Gimenes M.L., Vieira M.G.A., Silva M.G.C., 2017, Equilibrium study of cadmium ions adsorption on sericin/alginate particles, Chemical Engineering Transactions, 56, 1891-1896 DOI:10.3303/CET1756316

The objective of this study was to investigate the use of sericin/alginate particles as bioadsorbent to remove cadmium ions (Cd^{2+}) through adsorption equilibrium study using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models.

2. Materials and Methods

2.1 Preparation of the Particles

The *Bombyx mori* silkworm´s cocoons were kindly provided by Bratac Silk Mills Company, located in the State of Paraná – Brazil.

Methods for preparation of cocoons, extraction of sericin and higher molecular weight sericin fractionation were performed according to Silva et al., 2014. The concentration of sericin was determined and then adjusted to 25 g/L (2.5 % w/V). To obtain the blend, commercial sodium alginate (Sigma-Aldrich, UK) was incorporated at a ratio of 2 % w/V in the adjusted sericin solution with constant stirring.

The particles were prepared by ionic gelation process, where the blend was dripped, with a peristaltic pump (Masterflex L/S, 77800-60, USA), in aqueous solution of $CaCl_2$ (3 % w/V). At the end of this process, the particles formed were kept in constant agitation in the calcium chloride solution for 12 h to complete the crosslinking process. Subsequently, the particles were dried at room temperature and then kept in a continuous flow oven at 100 °C for 24 h for the thermal crosslinking to occur, in order to improve the mechanical properties of the particles.

2.2 Adsorption Equilibrium

Adsorption isotherm assays were conducted to determine the influence of temperature on the adsorption of cadmium ions on sericin/alginate particles. In these experiments, 0.5 g of particle was added to 50 mL cadmium ions solutions, which concentration ranged from 0.02 - 7 mmol/L. The system was stirred at 250 rpm at temperatures of 10 °C, 20 °C, 40 °C and 60 °C using a shaker to ensure homogeneity and contact the solution with the particles for 24 h. After this time, mixture was centrifuged to separate the supernatant and adsorbent. The concentration of Cd^{2+} ions in the supernatant was measured using an atomic absorption spectrophotometer (Shimadzu, AA-7000, Japan). The quantity of Cd^{2+} ions adsorbed at equilibrium was calculated by Eq(1):

$$q_e = \frac{(C_0 - C_e).V}{m} \tag{1}$$

where C_0 is the initial concentration of Cd^{2+} ions (mmol/L), C_e is the equilibrium concentration of Cd^{2+} ions (mmol/L), V is the volume of the solution (L) and m is the mass of the particles (g).

In the present study, Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption isotherm models were fitted to the adsorption equilibrium data.

2.2.1 Langmuir Isotherm

Langmuir isotherm equation assumes monolayer adsorption on a uniform surface with finite number of identical adsorption sites (Langmuir, 1918). The form of the Langmuir isotherm model is described as in Eq(2):

$$q_e = \frac{q_{max(L)} K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e is equilibrium capacity (mmol/g), C_e is the equilibrium concentration (mmol/L), K_L is the Langmuir constant related to the energy of adsorption (L/mmol) and $q_{\max(L)}$ is the maximum adsorption capacity (mmol/g).

The essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor, R_L, defined by the Eq(3):

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

Values of R_L indicate the type of Langmuir isotherm: irreversible (R_L = 0), favorable (0 < R_L < 1), linear (R_L = 1) or unfavorable (R_L > 1).

2.2.2 Freundlich Isotherm

The empirical Freundlich equation, Eq(4) considers the existence of a multilayer structure (heterogeneous surfaces) and assumes that the concentration of adsorbate on the adsorbent surface increases with the concentration of the adsorbate (Freundlich, 1906):

$$q_e = K_F {C_e}^{1/n} \tag{4}$$

where K_F (L/mmol) and n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity. The adsorption is favorable when n is in the range 1 - 10.

2.2.3 Dubinin-Radushkevich Isotherm

The Dubinin–Radushkevich (D–R) isotherm (Dubinin and Radushkevich, 1947) is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant sorption potential. D–R's equation as shown in Eq(5) is:

$$q_e = q_{\max(DR)} exp\left[-K_D\left(RTln(1+1/C_e)\right)^2\right] \tag{5}$$

where R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), K_D is the D–R constant (mol^2/kJ^2) and $q_{\max(DR)}$ is the maximum adsorption capacity (mmol/g).

The mean free energy of adsorption per molecule of the Cd^{2+} ions can be evaluated from Eq(6):

$$E = \frac{1}{\sqrt{2K_D}} \tag{6}$$

This parameter gives information about chemical or physical adsorption. With the magnitude of E between 8 and 16 kJ.mol^{-1}, the bioadsorption process follows chemical ion-exchange, while for the values of $\mathrm{E} < 8$ kJ.mol^{-1}, the bioadsorption process is of a physical nature.

2.2.4 Temkin Isotherm

The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent–adsorbate interactions (Temkin and Pyzhev, 1940). The linear form of Temkin isotherm model is given by the Eq(7):

$$q_e = \frac{RT}{b} lnK_T + \frac{RT}{b} lnC_e \tag{7}$$

where b is the Temkin constant related to the heat of sorption (kJ/mol) and $\mathrm{K_T}$ is the Temkin isotherm constant (L/mmol).

3. Results and Discussion

Figure 1 shows the experimental data of adsorption isotherms Cd^{2+} ions by the sericin/alginate particles. It can be seen that the adsorption capacity of Cd^{2+} ions by adsorption onto particles is favourable at low temperatures. This may be due to a tendency of the Cd^{2+} ions to escape from the solid phase to the bulk phase with an increase in the temperature of the solutions. This effect suggests that an explanation of the adsorption mechanism associated with the removal of Cd^{2+} ions involves a physical process, which is usually associated with low adsorption heat (Azouaou et al., 2010).

Isotherms exhibit the same behaviour for all temperatures, which indicates the adsorption is favourable according to classification of McCabe (1993) as shown in Figure 1.

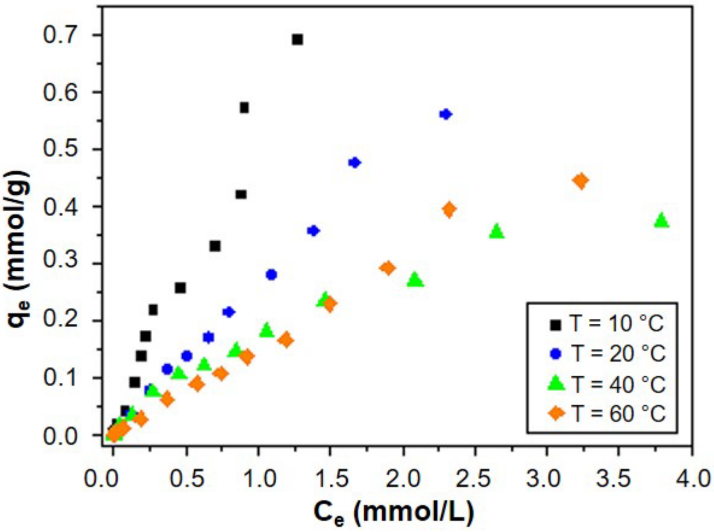

Figure 1: Effect of temperature on the Cd^{2+} adsorption capacity on sericin/alginate particles

To evaluate the isotherms models and its capabilities to fit to the experimental data, the graphs for each isotherm were plotted for four different temperatures evaluated: 10 °C (a), 20 °C (b), 40 °C (c) and 60 °C (d), which are shown in Figure 2.

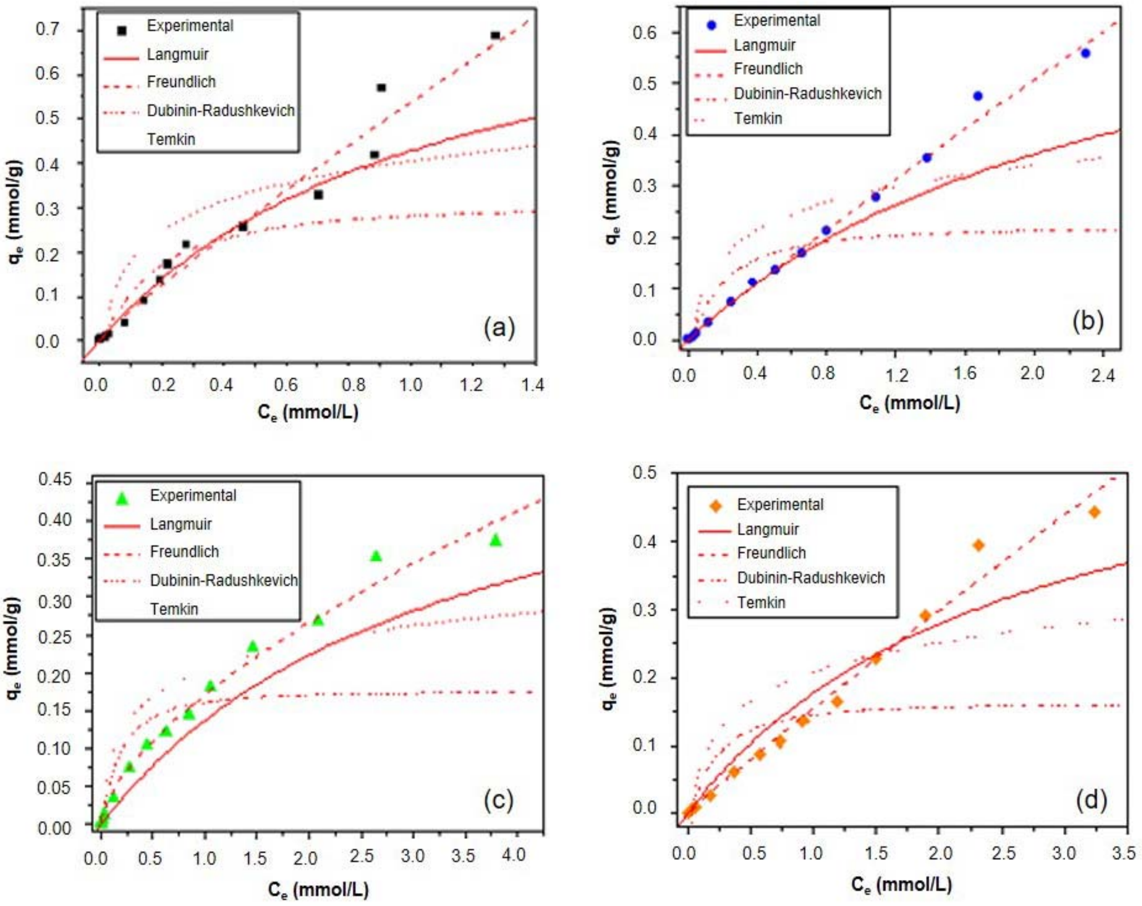

Figure 2: Experimental and adjusted isotherms for adsorption of cadmium on sericin/alginate particles at different temperatures: (a) T = 10 °C; (b) T = 20 °C; (c) T = 40 °C and (d) T = 60 °C

The best fit among the isotherm models is assessed by the linear coefficient of determination (R^2) and average relative error (ARE). The average relative error test measures the difference between the experimental and model data. If data from the model are similar to experimental data, ARE numbers will be small. The adsorption constants for each model with correlation coefficients and average relative error are represented in Table 1.

By comparing the coefficient of determination (R^2), it was found that Langmuir and Freundlich isotherms represent good models for the adsorption system. However, the Freundlich model, which predicts the heterogeneity of the adsorption sites, is a better fit to the experimental data at all temperatures evaluated because it presented lower values of average relative error (ARE). According to Figure 2, the Dubinin-Radushkevich and Temkin models provide a good fit to the experimental data concerning low equilibrium concentrations.

Regarding to the parameters, the values of the dimensionless parameter RL of the Langmuir model lay between 0 and 1, indicating a favourable adsorption. The RL values increased with increasing temperature, wherein the highest value was obtained for temperature of 40 °C. The Freundlich model is usually applied to adsorption on heterogeneous surfaces strongly. The values of n are greater than unity, indicating that the Cd^{2+} ions are favourably adsorbed by sericin/alginate particles at all temperatures studied.

The activation energy (E) results estimated by the Dubinin-Radushkevich model were low (< 8 kJ/mol) for all temperatures measured, indicating that the adsorption process is physical. This indicates the possibility of desorption of metal ion adsorbed on the particles sericin/alginate. The heat of adsorption values (b) of Temkin isotherm for the systems studied were found to be less than 8 kJ/mol, which also indicates that a weak interaction between the Cd^{2+} ions and the adsorbent.

The cadmium adsorption capacity on sericin/alginate particles obtained by the Langmuir model at about room temperature (20 °C) was 0.8312 mmol Cd^{2+}/g particle (or 93.44 mg Cd^{2+}/g particle). This is higher than the adsorption capacity of other alternative adsorbents reported in the literature: coffee grounds (15.65 mg/g) (Azouaou et al., 2010); chestnut shell (4.07 mg/g) (Vásquez et al., 2009) and Eucalyptus seeds (71.15 mg/g) (Kiruba et al., 2014). It shows the potential use of this adsorbent for the removal cadmium ions at low concentrations.

Table 1: Langmuir, Freundlich, D–R and Temkin isotherm model parameters for adsorption of cadmium on sericin/alginate particles

Isotherm	Parameters	Temperature (ºC)			
		10	20	30	40
Langmuir	$q_{max(L)}$ (mmol/g)	0.8926	0.8312	0.5944	0.6446
	K_L (L/mmol)	0.9195	0.3872	0.2991	0.3809
	R_L	0.1384	0.2760	0.3305	0.2793
	R^2	0.9832	0.9976	0.9921	0.9984
	ARE (%)	34.5296	12.2885	22.4210	8.0539
Freundlich	K_F (L/mmol)	0.5381	0.2643	0.1707	0.1548
	n	1.1050	1.0642	1.5707	1.0529
	R^2	0.9801	0.9935	0.9877	0.9866
	ARE (%)	32.5488	11.8199	13.1275	5.1130
Dubinin-Radushkevich	$q_{max(D-R)}$ (mmol/g)	0.3065	0.2207	0.1756	0.1625
	K_D (mol^2/kJ^2)	0.0331	0.0362	0.0269	0.0306
	E (kJ/mol)	3.8859	3.7174	4.3105	4.0435
	R^2	0.9036	0.8955	0.9118	0.8733
	ARE (%)	39.0353	34.2106	45.6939	30.7564
Temkin	K_T (L/mmol)	6.5039	4.0336	5.8942	2.7092
	b (kJ/mol)	7.7164	6.9807	6.8725	5.8541
	R^2	0.8729	0.9098	0.9227	0.9081
	ARE (%)	51.9633	32.8637	35.2278	34.6883

4. Conclusions

Sericin/alginate particles were investigated as adsorbents for the removal of cadmium ions from aqueous solutions through equilibrium study. It was found that temperature is an important factor influencing this adsorption process, wherein adsorption capacity increases with decreasing temperature, which demonstrates that low temperatures are more favourable. Equilibrium isotherms were evaluated using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models. Freundlich model, which predicts heterogeneity of adsorption sites, provided the best fit to experimental data for all temperatures (10 °C, 20 °C, 40 °C and 60 °C). The values of n are greater than unity, indicating that the Cd^{2+} ions are favourably adsorbed by sericin/alginate particles. Results showed that the sericin/alginate particles have a high adsorption capacity and are comparable to some bioadsorbents. They also suggest that these particles can be used as effective bioadsorbents for the removal of Cd^{2+} in wastewater.

Acknowledgments

The authors thank the BRATAC Company for providing the silkworm cocoons, CNPq (Proc. 470615/2013-3 and 300986/2013-0), CAPES and FAPESP (Proc. 2015/13505-9) for financial support.

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