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C. hildmannianus Peel for Protein Adsorption

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This study aims was to evaluate the potential of *C. hildmannianus* peel as a protein biosorbent. The FTIR analysis showed the presence of peaks in the range of 3400-3300 cm^{-1} which can be attributed to hydroxyl groups of cellulose, pectin, hemicelluloses and lignin; CH_2 and CH_3 groups were present in the range of 2800-3000 cm^{-1}, and COC groups in 1200-1000 cm^{-1} interval. The point of zero charge (pH_{pcz}) was found at the pH 4.54. The adsorption efficiency was investigated by kinetic adsorption tests. There was a concentration decrease in the solution to 0.476 mg L^{-1} until the equilibrium for the highest concentration studied (1.0 mg L^{-1}), corresponding to 52.4 % decrease of the initial concentration. The experimental data were well described by a pseudo-second order diffusion model with determination coefficients varying from 0.966 to 0.981. The adsorption capacity increased with temperature increasing indicating an endothermic process and chemisorption. This is evidenced by the long time required to reach equilibrium, 12 – 24 h, for three concentrations of BSA solutions studied. Equilibrium adsorption isotherms were satisfactorily described by Langmuir model. Values of equilibrium parameter constant, $R_{L,}$ were found to be $0 < R_L < 1$ and confirmed that the *C. hildmannianus* is favorable for adsorption of BSA under the conditions studied. It can be concluded that the adsorbent studied has good perspective to be used as adsorbent material in protein removal from food industry wastewaters since it has a good adsorption capacity (ranged from 360.5 to 554.5 mg g^{-1}).

1. Introduction

Discharge of effluents generated by the agriculture and food industries is a major environmental problem worldwide (Lopez-Fiuza et al., 2002). Waste from food industries are highly variable in composition and can include solid and liquid with organic substances as fats, proteins and carbohydrates, in addition to chemical residues from both processing as cleaning procedures. Typically, these wastes cause no risk and are biodegradable, however the amount generated and its high content of organic matter can cause serious environmental problems if they do not receive any treatment before disposal in receiving bodies (Hayes, 1995).

Wastewater treatment is becoming ever more critical due to the increasing scarcity of the water resources and wastewater disposal costs; stricter discharge regulations have also lowered permissible contaminant levels in waste streams (Ferrero and Periola, 2011).

Adsorption techniques employing solid adsorbents are effective methods for water decontamination. Some natural biomaterials from agricultural products and other low costs by-products have been explored as new sources of sorbents in recent years.

The *Cereus hildmannianus* K. Schum is a cactus species occurring naturally in arid regions of Brazil. Its edible fruit is mainly constituted by mucilage, a complex carbohydrate considered as dietary fiber. The recent possibility of industrial processing of this fruit generates significant amounts of waste. A very little data are found in literature about the use of this plant as adsorbent, exception to Gilioli et al. (2012). The objective of this study was to evaluate the potential of *C. hildmannianus* peel in adsorption of protein, one of the most abundant compounds existing in the food industry residues. Bovine Serum Albumin (BSA) was used as model protein since it is readily available in highly purified form in the market and literature is rich on investigations of its adsorption on a range of materials.

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2. Materials and Methods

2.1 Preparation of Adsorbent and BSA solution

The fruit *Cereus hildmannianus* K. Schum*,* popularly known as Tuna, was directly obtained from the agriculturist from Zortéa, Santa Catarina, Brazil. The peel, residue of the juice process, was extensively washed with water to remove impurities, sprayed with distilled water and dried at 60 ^{o}C until constant weight. Dried biomass was crushed, sieved, and maintained under dried atmosphere until use. Bovine Serum Albumin (BSA - SIGMA) was prepared in distilled water.

2.2 Adsorbent Characterization

FTIR spectroscopy was used to identify the chemical groups in the adsorbents. An FTIR spectrum of the adsorbent was recorded from 400 to 4000 cm^{-1} using a Shimatzu model IR PRESTIGE-21 in KBr discs.
The point of zero charge (pH_{pzc}) was evaluated according to the methodology of Faria et al (2004) with some modifications (Vandresen, 2011).

2.3 Adsorption Experiments

The adsorption studies were carried under controlled temperature and agitation, and pre-established pH values and BSA concentrations. Samples of uniform particle size and constant weight of the adsorbent were added to known volumes of BSA solutions. The equilibrium was investigated within the time interval varying from 0 to 48 h. The isotherm adsorptions assays were performed at temperatures of 298, 318 and 338 K; Langmuir and Freundlich isotherms were fitted to the equilibrium adsorption data. After the equilibrium was attained, the samples were centrifuged and the protein content was determined in the supernatants by the method of Bradford (1976), using UV–vis Spectrophotometer (T-90+ PG Instruments Ltd.) where the absorbance value was acquired at 595 nm. All the experiments were duplicated.
The amount of BSA adsorbed by *C. hildmannianus* peel (q_e (mg g^{-1})) was calculated by a mass balance according to Equation 1 (Demir et al., 2008):

$$q_e = (C_0 - C_e)V/M \qquad (1)$$

where
C_0: initial liquid phase concentration of BSA (mg L^{-1}),
C_e: equilibrium liquid phase concentration of BSA (mg L^{-1}),
V: volume of the solution (L),
M: mass of the adsorbent employed (g).

3. Results

3.1 Adsorbent Characterization

The infrared spectroscopy for the adsorbent is shown in Figure 1. The broad and intense absorption band at 3417 cm^{-1} corresponds to O-H and N-H stretching vibrations; in this kind of material they regard to cellulose, pectin, hemicellulose, lignin and absorbed water. The band around 2919 cm^{-1} can be attributed to C-H stretching vibrations of methyl, methylene and methoxy groups. The presence of the bands at 1735 cm^{-1} and 1641 cm^{-1} in the spectrum indicates the stretching bands of ester carbonyl (C=O) groups and carboxylate ion (COO^-), respectively (Perez-Marin et al., 2007). The point of zero charge (pH_{pzc}) of the adsorbent was at pH 4.54. Thus, the adsorption of cations is favored at pH > $pH_{pcz,}$ because in that pH values the adsorbent surface is negatively charged attracting the cationic adsorbates. At pH < pH_{pcz} adsorption of anions is favored.

3.2 Adsorption Experiments

The kinetics results of the adsorption process are shown in the Figure 2 (a). The adsorption capacity of the *C. hildmannianus* peel ranged from 360.5 to 554.5 mg g^{-1} for the three initial concentrations evaluated. The initial concentration decreased from 1.0 mg L^{-1} to 0.476 mg L^{-1} in the solution when the equilibrium was attained, corresponding to approximately 52.4 %. Although the kinetics have been conducted up to 48 hours, no significant changes were observed after 24 h, indicating that the equilibrium was reached between 12 to 24 h.

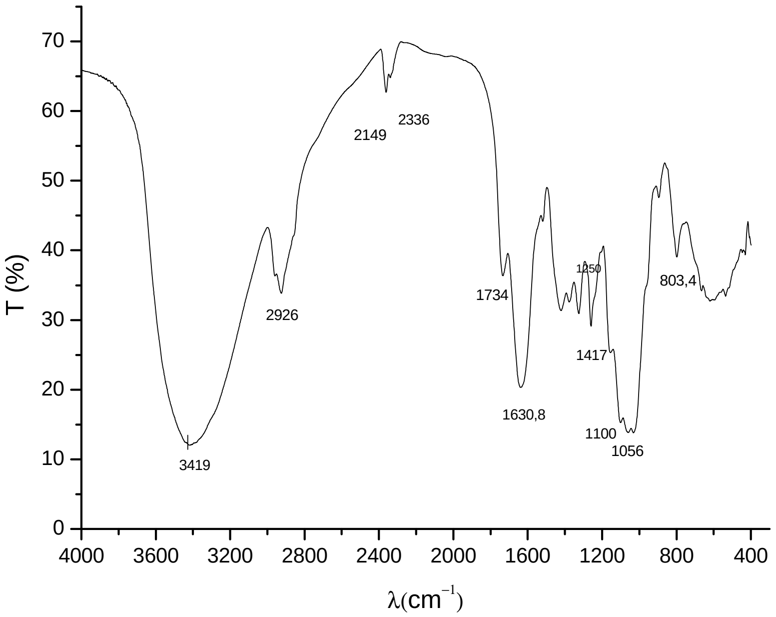

Figure 1: FTIR spectra of Cereus hildmannianus peel.

The experimental results were fitted by a second-order kinetic model (Equation 2). Results are shown in Figure 2 (b).

$$t / q_t = 1 / (k_2 \, . q_e^2) + (1 / q_e).t \qquad (2)$$

where q_e is the amount of protein adsorbed at the equilibrium time (mg g^{-1}); q_t is the amount adsorbed at time t (mg g^{-1}); k_2 is the second order rate constant (g mg^{-1} min^{-1}).

Kinetic parameters calculated for pseudo-second-order are shown in Table 1. The values of the determination coefficient (R^2) varied from 0.966 to 0.981 to the experiments performed. It is observed that the values of k_2, the second order rate constant, was higher for the lower concentration (0.6 mg mL^{-1}), since the higher the adsorption rate constant, the faster the process (Vandresen, 2011).

Table 1: Pseudo-second-order kinetic parameters for BSA adsorption by C. hildmannianus peel

Concentration (mg mL^{-1})	$q_{e,exp}$ (mg g^{-1})	k_2 (x 10^{-5}) (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	h (mg g^{-1} min^{-1})	R^2
0.6	496.1	0.771	591.7	2.699	0.978
0.8	360.5	2.490	384.6	3.683	0.981
1.0	554.5	5.490	300.3	4.950	0.966

The adsorption isotherms give very important informations about the solute-solvent interaction, and are very useful for the optimization of the adsorbents characteristics. Figure 3 (a) presents the experimental biosorption isotherm for BSA on *C. hildmannianus* peel for the initial concentrations of BSA varied from 0.6 to 1.2 mg/mL at 298, 318 and 338 K.

It is observed in Figure 3 (a) that the adsorption capacity increased with the temperature increasing indicating an endothermic process. A decrease in the amount adsorbed with increasing temperature may be indicative of a physical adsorption process. The opposite is generally true for chemisorption (Nassar and Magdy, 1997).

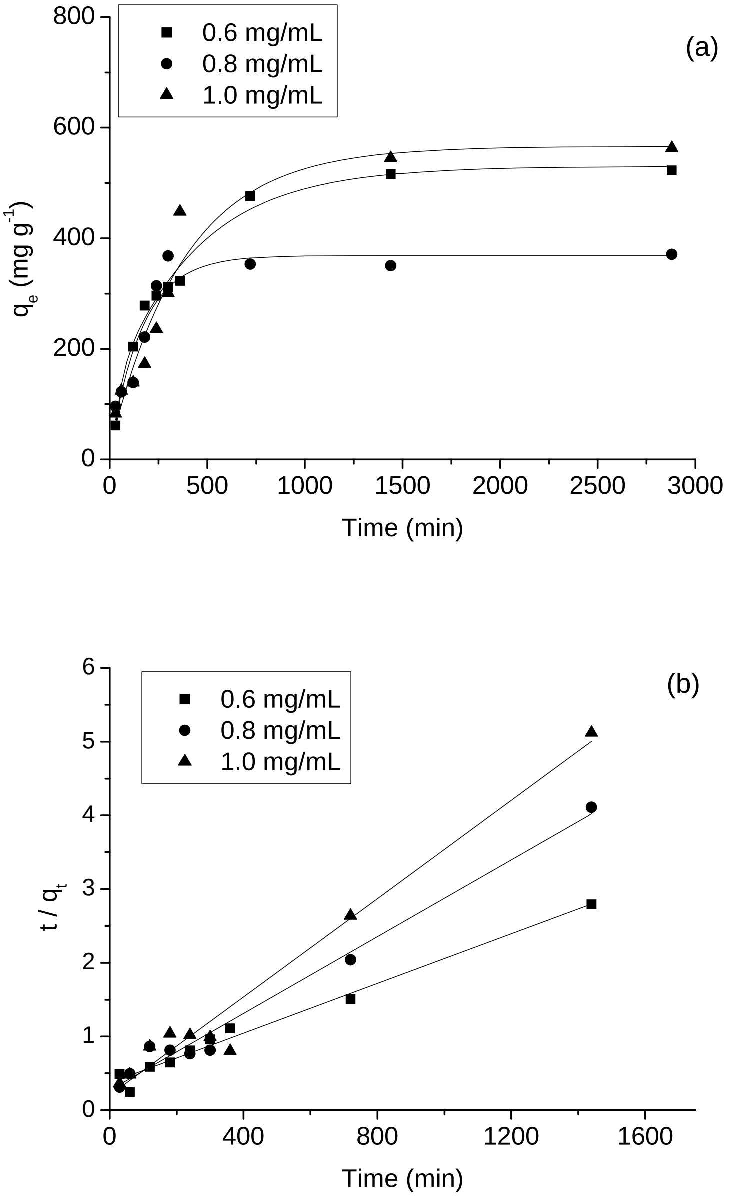

Figure 2: (a) Adsorption kinetics of BSA on C. hildmannianus peel at 298 K.; (b) Fitting of a pseudo-second-order model for the adsorption kinetics.

The chemical adsorption involves much stronger interaction between the solid adsorbent and the substance adsorbed. This type of adsorption results from an important electron transfer; it is equivalent to the formation of a chemical bond between the adsorbate and the solid surface. Such interactions are stronger and more specific than the forces of physical adsorption, and are limited to the monolayer coverage.

Langmuir and Freundlich are the two isotherm models most used to describe equilibrium data. The equilibrium adsorption isotherms presented here were satisfactorily described by the Langmuir model. Figure 3 (b) illustrates the Langmuir description for the case at 298 K.

The essential characteristics of Langmuir isotherm can be expressed by the dimensionless equilibrium parameter, R_L, which is expressed by Equation 3 (Weber and Chakkravorti, 1974). The R_L value indicates the irreversibility degree of the isotherm, which can be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of R_L were found to be 0.04, 0.093 and 0.132, at

298, 318 and 338 K, respectively, and confirmed that the *Cereus hildmannianus* is favorable for adsorption of BSA under the conditions studied.

$$R_L = 1 / (1+bC_0) \qquad (3)$$

where C_0 is the initial solution concentration (g L^{-1}) and b (L g^{-1}) is the Langmuir constant.

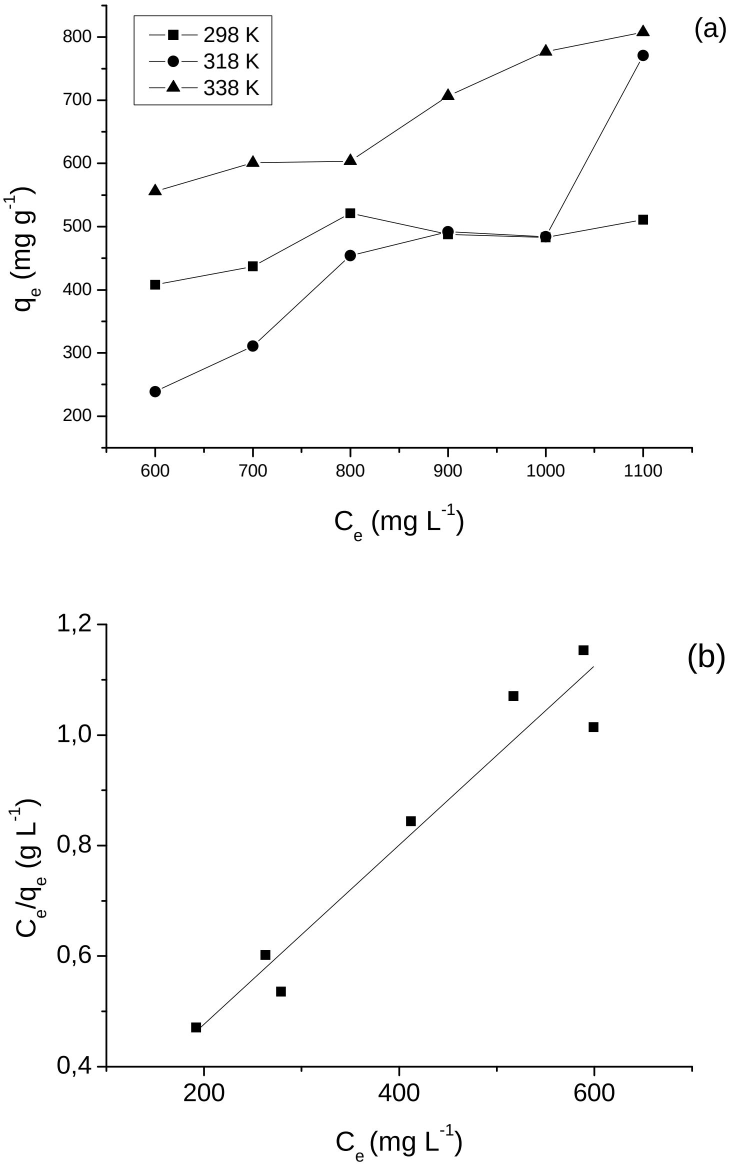

Figure 3: (a) Experimental adsorption isotherms for BSA on Cereus hildmannianus peel. (b) Langmuir isotherm fit at 298 K.

4. Conclusions

The *Cereus hildmannianus* peel has good perspectives to be used as adsorbent material in protein removal from food industry wastewaters. The adsorbent studied presented high adsorbent capacity despite its slow adsorption kinetics, since protein concentration was reduced 54% by the adsorbent in the highest concentration condition. The kinetics experimental data were well described by a pseudo-second order diffusion model and the equilibrium was satisfactorily represented by the Langmuir model.

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