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Adsorption of Emerging Pollutant by Pecan Shell-Based Biosorbent

Sabrina Grando Cordeiro [1], Ani Caroline Weber [1], Bruna Costa [1], Bruno Rampanelli Dahmer [1], Daniel Kuhn [1], Eduardo Miranda Ethur [1], Valeriano Antonio Corbellini [2] and Lucélia Hoehne [1,*]

[1] Graduate Program in Biotechnology, University of Taquari Valley-Univates, Lajeado 95900-000, RS, Brazil
[2] Department of Physics and Chemistry, University of Santa Cruz do Sul-UNISC, Santa Cruz do Sul 96815-900, RS, Brazil
* Correspondence: luceliah@univates.br

Abstract: The insertion of antibiotics in water resources results from anthropogenic sources; however, at residual concentrations, they characterize potential risks to the ecosystem, such as the emergence of multi-resistant bacteria. It is necessary to develop technologies to provide sustainable solutions for low- and middle-income countries. Thus, the present study aims to evaluate the ability to remove the antibiotic ciprofloxacin (CPX) with a biosorbent produced with pecan shells (PSB). The PSB structure was determined by scanning electron microscopy and spectroscopy in the infrared region by Fourier Transform. For adsorption assays, solutions of 10 mg L^{-1} of CPX were used. The results show that the process reaches equilibrium at 240 min, and follows the pseudo-second order model kinetic and the Freundlich equilibrium model. The increase in temperature and the pH variation of the solution strongly influence the process. In general, the adsorption of CPX using PS is a potential method for treating water and contaminated effluents, as well as being a low-cost method; this is because it uses a byproduct from the agricultural industry that results in a reduction of approximately 60% of the antibiotic load contained in the liquid effluent.

Keywords: activated charcoal; adsorption; antibiotic; biosorbent; ciprofloxacin; pecan shells

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1. Introduction

Recently, the production and consumption of different classes of antibiotics in human and veterinary medicine has been increasing greatly [1]. Due to the low percentage of metabolism in the body (10–50%) a significant portion of antibiotics and their metabolites is excreted through urine and feces in their unaltered form. Antibiotics access the environmental matrices without any restrictions because of the inefficiency of wastewater treatment plants (WWTPs) in completely eliminating this class of contaminants, which are called emerging pollutants [2,3]. Although the access of antibiotics to aquatic matrices occurs at trace levels (μg L^{-1} and ng L^{-1}), the continuous introduction of this type of contaminant in the environment poses potential risks to both humans and the environment due to its cumulative effect [4]. The presence of this class of microcontaminants may result in several endocrine disturbances to the local flora and fauna, increased toxicity in the environment, and the presence of antibiotics in aqueous matrices; these leads to the emergence and perpetuation of multidrug-resistant pathogen genes [5].

Fluoroquinolones (FQs) are a class of synthetic antibiotics widely used in human, veterinary, and aquaculture medicine due to their broad spectrum of antimicrobial action and the inhibition of the DNA gyrase of bacteria as a mechanism of action; this results in a fast antibacterial action. Among the most used FQs, ciprofloxacin (CPX) stands out. Its average annual prescription is 33,000 kg, resulting in a wide distribution of this contaminant in environmental matrices [6]. CPX has already been identified in surface waters at concentrations of 1.56–7.14 ng L^{-1}, in hospital wastewater at concentrations of 8.95 ng L^{-1} [7] and in WWTPs at concentrations of 185–613 ng L^{-1} [8]. Numerous toxic and

mutagenic effects of the presence of this pollutant have been reported, such as oxidative stress and cellular damage; this may lead to neurotoxic damage in *Daphnia magna* [9], in addition to being associated with the possibility of inhibiting the photosynthesis of some plants, thus resulting in morphological abnormalities [2,6].

Due to this reality, many efforts have been made in an attempt to develop viable and effective methodologies for the removal of this class of contaminants from water resources, or for its degradation. Currently, adsorption is one of the most applied procedures because of its wide versatility of application, high efficiency, low toxicity, and ease of processing and operating [10,11]. Developing Latin American countries are major producers of agricultural products. Brazil, for example, with its vast agricultural production, generates around 298 million tons of bio-waste, originating from sugarcane, rice, soybean, and wheat crops. These bio residues are often underestimated, which ignores the fact that this huge amount of agro-industrial waste can serve another purpose in the industry [12].

Thus, the present work aims to develop and characterize a biosorbent produced from agro-industrial waste of pecan (*Carya illinoinensis*), extremely common in Brazil, in this case its shells, to explore the adsorption capacity against the antibiotic CPX in an aqueous matrix, analyze its parameters (pH, temperature, contact time, and CPX concentration), and investigate adsorption mechanisms.

2. Materials and Methods

2.1. Adsorbate

Ciprofloxacin (CPX, $C_{17}H_{18}FN_{33}$·HCl, 98%, CAS: 85721-33-1) was purchased from Sigma Aldrich (Jerusalem, Israel), and the stock solution was prepared by solubilization of the compound in methanol with 10% NaOH, both from Merck (Berlim, Germany).

2.2. Adsorbent

The methodology adopted for the production of the adsorbent was adapted from the literature [13]. The pecan shells (PS) used in the study were kindly provided by the Pitol Group (Anta Gorda, Rio Grande do Sul, Brazil). The shells were washed repeatedly with warm deionized water, dried in an oven at 50 °C for 48 h, and crushed in a hammer mill. To prepare the biosorbent (PSB), granulometric fractions between 710 and 1000 µm were selected. The fractions were previously burned in a muffle furnace at 600 °C for 3 h, with a subsequent chemical activation by immersion in zinc chloride ($ZnCl_2$ 50%, Synth, Brazil, PN:solution 1:8 m/v) for 24 h under stirring, and thermal activation through sample pyrolysis in a muffle furnace with nitrogen flow at 600 °C for 3 h. After the heat treatment, the sample was washed repeatedly with a 0.05 mol L^{-1} hydrochloric acid (Synth, Brazil) solution to remove the remaining $ZnCl_2$ and the deionized water for neutralization. The yield (Y_{PS}) of the PSB was calculated by Equation (1).

$$Y_{PS}(\%) = \frac{W_{PS}}{W_{WS}} \times 100 \quad (1)$$

where W_{PS} and W_{WS} are the mass of the resulting activated charcoal and the mass of pecan shells used to prepare the PSB, respectively. The morphological characterization of the surface of PSB and PS was observed through scanning electron microscopy (SEM) (Carl Zeiss LS-10, Berlin, Germany). The organic groups present on the surface of PS and PSB were studied by acquiring the spectra in triplicate using attenuated total reflectance in a Fourier transform infrared spectrometer (FT-IR/FT-NIR) (Spectrum 400 Spectrometer from Perkin-Elmer, Waltham, MA, USA).

2.3. Batch Adsorption

The adsorption assays were conducted in 250 mL conical flasks containing 100 mL of CPX solution (10 mg L^{-1}) and 200 mg of PSB. Although the concentration of CPS used does not mimic the real concentrations of the antibiotic usually identified in environmental matrices (µg L^{-1} to ng L^{-1}), this value was used in order to adjust the parameters in the

adsorption process, thus, the possibility of utilizing PSB for the removal of CPX could be assessed, before proceeding to tests with lower concentrations and closer to reality The mixture was constantly stirred at 170 rpm on an orbital table (Tecnal TE-140, Piracicaba, São Paulo, Brazil) for a predetermined time. The parameters studied were pH (3–10), contact time (5 to 360 min), initial CPX concentration (2–10 mg L^{-1}), and solution temperature (10–50 °C). The studies were carried out at an initial pH of 6 at room temperature (23 ± 2 °C). After the predefined contact time, the samples were filtered with a 22 µm membrane, and the final CPX concentration was determined using a molecular absorption spectrophotometer in ultraviolet-visible (Thermo Scientific, USA) at a wavelength of 272 nm.

The values of adsorption capacity (q_e, mg g^{-1}) of the PSB at equilibrium and the removal percentage (%) of ciprofloxacin by the pecan shell biosorbent were obtained using the following equations:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

$$\%\ Removal = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

where C_0 and C_e (mg L^{-1}) are the initial concentration and the CPX equilibrium in the solution, respectively. W (g) is the mass of PSB added to the solution, and V (L) is the solution volume.

To understand the process' thermodynamics, the parameters Gibbs Free Energy variation (ΔG, kJ mol^{-1}), entropy variation (ΔS, kJ mol^{-1}), and enthalpy variation (ΔH, kJ mol^{-1}) were calculated according to the following equations:

$$lnK_d = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature of the solution (K), and K_d is the thermodynamic equilibrium constant (dimensionless), which can be obtained through the ratio between the CPX concentration at equilibrium and the adsorption capacity at equilibrium [14]. The adsorption capacity was estimated using the linearized form of equilibrium (isothermal) and kinetic models, as Table 1 shows.

Table 1. List of the equilibrium and kinetic models.

	Model	Equation	Variables	References
Kinetic models	Pseudo-first order	$\frac{\partial q}{\partial t} = k_1(q_e - q)$	q_e; k_1	[15]
	Pseudo-second order	$\frac{\partial q}{\partial t} = k_2(q_e - q)^2$	q_e; k_2	[15]
	Elovich	$\frac{\partial q}{\partial t} = k_2(q_e - q)^2$	α; β	[16]
Equilibrium models	Langmuir	$q_e = \frac{q_{max}K_LC_e}{1+K_LC_e}$	q_{max}; K_L	[17]
	Freundlich	$q_e = K_f(C_e)^{\frac{1}{n}}$	K_f; n	[17]

3. Results and Discussion

3.1. Characterization of the Biosorbent

The yield (Y_{PS}) of the biosorbent after the physical and chemical processes for pecan shell activation was 33.6%. The FT-IR analysis was conducted for pecan shell samples *in natura* (PS), biosorbent (PSB), microcrystalline cellulose, and the two samples of commercial activated charcoal, one of which is powdered coal (CAP) and the other is granular charcoal (CAG), for comparison purposes. Figure 1 shows the spectra.

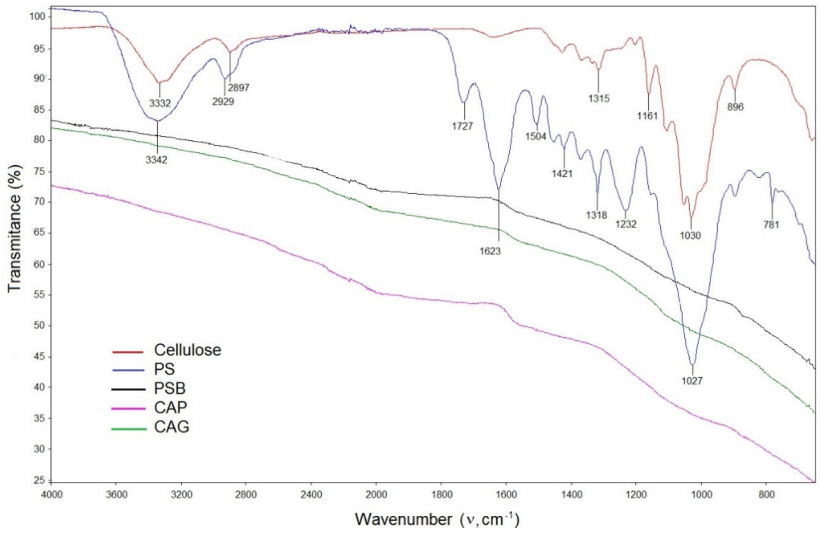

Figure 1. Characterization of the biochar via FT-IR for the PS, PSB, CAP, CAG and cellulose.

The PS sample is characteristic of lignocellulosic materials. It presents typical bands of materials with high cellulose (it can be compared to that obtained for microcrystalline cellulose) and hemicellulose contents. The manifestation of a broadband at 3342 cm^{-1} sugests the presence of alcoholic and phenolic hydroxyl νO-H involving hydrogen bonds; at 2929 cm^{-1}, it suggests the presence of alkyl νC-H. The 1027 cm^{-1} band can be attributed to the elongation of νC-O bonds, which is characteristic of monosaccharide units. The bands at lengths of 1727 and 1623 cm^{-1} are characteristic of the carbonyls (νC=O) of ketone (1727 cm^{-1}) and aldehyde (1623 cm^{-1}), which make up lignocellulosic material structures. In addition, there are movements of aromatic rings (1421 and 1318 cm^{-1}), COC asymmetric vibration bands of lignin phenols (1232 cm^{-1}), and distension vibration in aromatic C=C bonds (1504 cm^{-1}) (Bykov, 2008). When observing the spectrum obtained in the analysis of the carbonized pecan shell (PSB), the bands present in the raw material disappear completely, indicating that the pyrolysis resulted in the oxidation of these compounds, this made the spectrum very similar to that of the patterns of CAP and CAG commercial charcoal.

In addition, the surface morphology of the material in natura and of the biosorbent was also monitored through micrographs using SEM (Figure 2a,b). It is possible to observe that the structure of the PS has a heterogeneous morphology without porosity. As for the PSB sample, the physical and chemical activations (with $ZnCl_2$) led to the development of micropores on the material surface. The activating agent, once incorporated in the precursor material, promotes dehydration or oxidation of some compounds present in the material; this results in the unblocking of pores and consequently in an adsorbent with a high porosity and a more carbonaceous and aromatic structure [18].

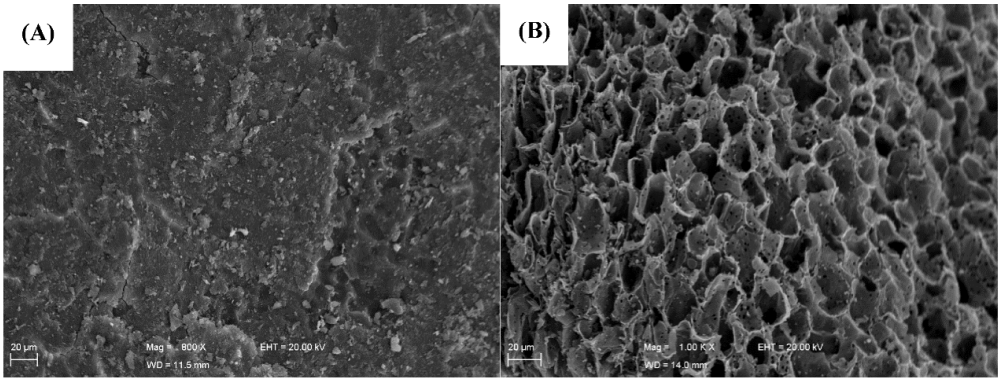

Figure 2. SEM micrographs (×800 and ×1000) of (**A**) an in natura pecan shell (PS); and (**B**) the biosorbent (PSB).

3.2. Biosorption Kinetics

The batch adsorption experiments initially determined the equilibrium time, where a fixed CPX concentration was used and the adsorption time varied from 5 to 360 min. Figure 3 shows the experimental results obtained for (A) % of removal and (B) amount adsorbed.

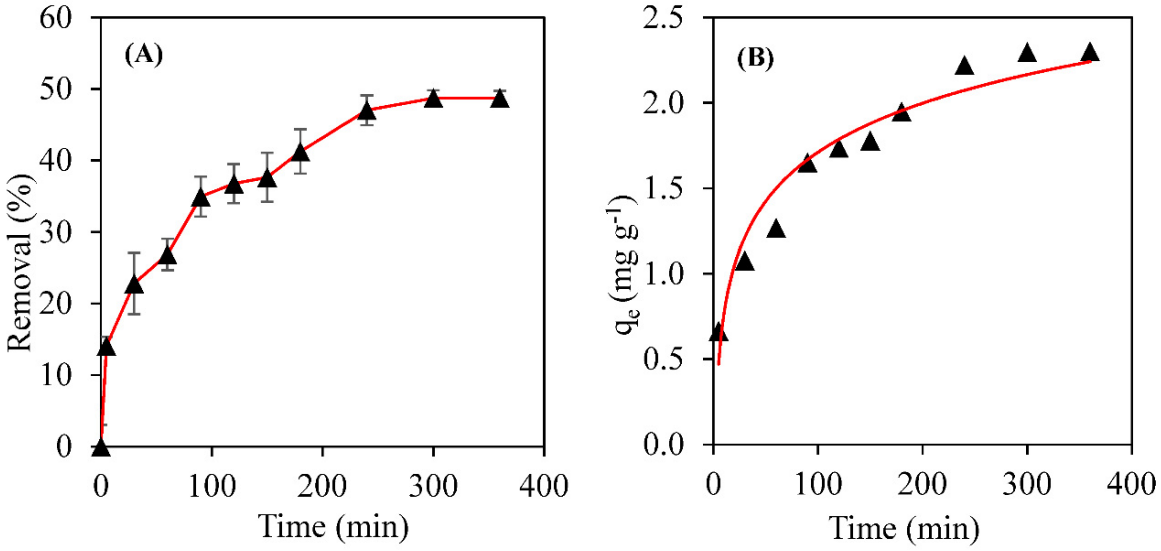

Figure 3. Equilibrium time for the CPX antibiotic. (**A**) the percentage of removal as a function of time; and (**B**) the amount adsorbed as a function of time.

It took approximately 240 min of contact for the system to reach an equilibrium. The removal percentage of the initial CPX concentration in this period was approximately 49%; this corresponds to ±2.30 mg of CPX per g of PSB. The adsorption speed is faster at the beginning of the process, while it gradually slows down at the end of the experiment until reaching an equilibrium. This adsorption behavior is due to the large number of empty and available active sites for adsorption at the beginning of the experiment. With the results of the equilibrium time, it was possible to create a mathematical modeling for the most frequently used kinetic models: pseudo-first order; pseudo-second order; and Elovich, which is calculated as expressed in Table 1. Figure 4 shows the linear graphs of each model, prepared in accordance with Avci (2020); Table 2 shows the calculated results.

Table 2. Kinetics model parameters and regression coefficients for ciprofloxacin the adsorption by biosorbent made of pecan shells.

Kinetics Model	Kinetics Model Parameter and Regression Coefficient		
Pseudo-first order	k_1 (h^{-1})	q_e (mg g^{-1})	R^2
	0.0155	2.19	0.8553
Pseudo-second order	k_2 (g mg h^{-1})	q_e (mg g^{-1})	R^2
	0.0082	2.25	0.9915
Elovich	β	α	R^2
	2.05	0.15	0.9391

As Table 2 shows, the pseudo-second order model best fits the experimental data, for it has the highest coefficient of correlation (R^2 = 0.9915). In addition, the calculated adsorption capacity (q_e = 2.25 mg g^{-1}) is close to the experimental adsorption capacity (q_e = 2.30 mg g^{-1}). The better fit to the experimental data by a second order model indicates that the adsorption is driven by a chemical-type reaction rate (chemisorption); this

suggesting that the sharing and the exchange of electrons on the surface of the biosorbent for the adsorption of ciprofloxacin is the mechanism that drives the process [10].

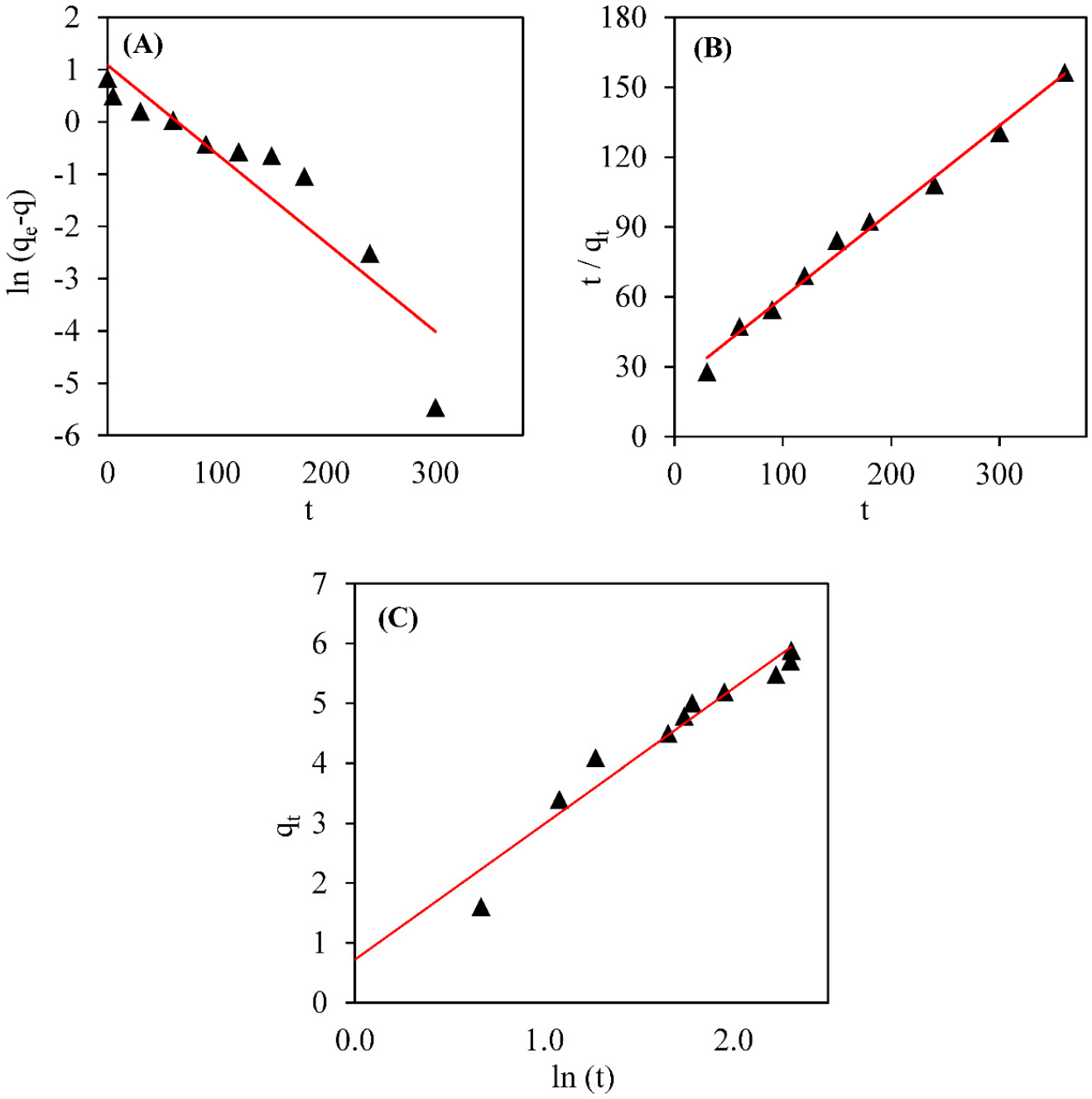

Figure 4. Linear plots of the (**A**) pseudo-first order kinetic model, (**B**) pseudo-second order kinetic model, and (**C**) Elovich model for ciprofloxacin adsorption by the biosorbent made of pecan shells.

3.3. Effect of pH and the Zero-Charge Point pH

The charges present on the adsorbent surface, as well as the charges of CPX in aqueous media, are strongly influenced by the pH of the solution [11]. Because of this, the influence of this parameter on the removal of CPX at different pH scales (2–10) was tested, and Figure 5 shows the results. The CPX has an amphoteric characteristic due to the presence of protonatable groups in its molecule; the behavior of CPX varies according to the medium pH. The antibiotic has two protonatable sites that establish dissociation constants (Figure 5a), defined as 5.09 (pKa_1). Below this value, it behaves as a cation; above 8.8 (pKa_2), it behaves as an

anion. Among these pH values, ciprofloxacin has a zwitterion characteristic (neutral species); it has both positively charged regions and negatively charged regions in its molecule [19]. In the experiment, the highest CPX removal rate (47%) was between pH 5 and 6; i.e., in the neutral pH range of the antibiotic.

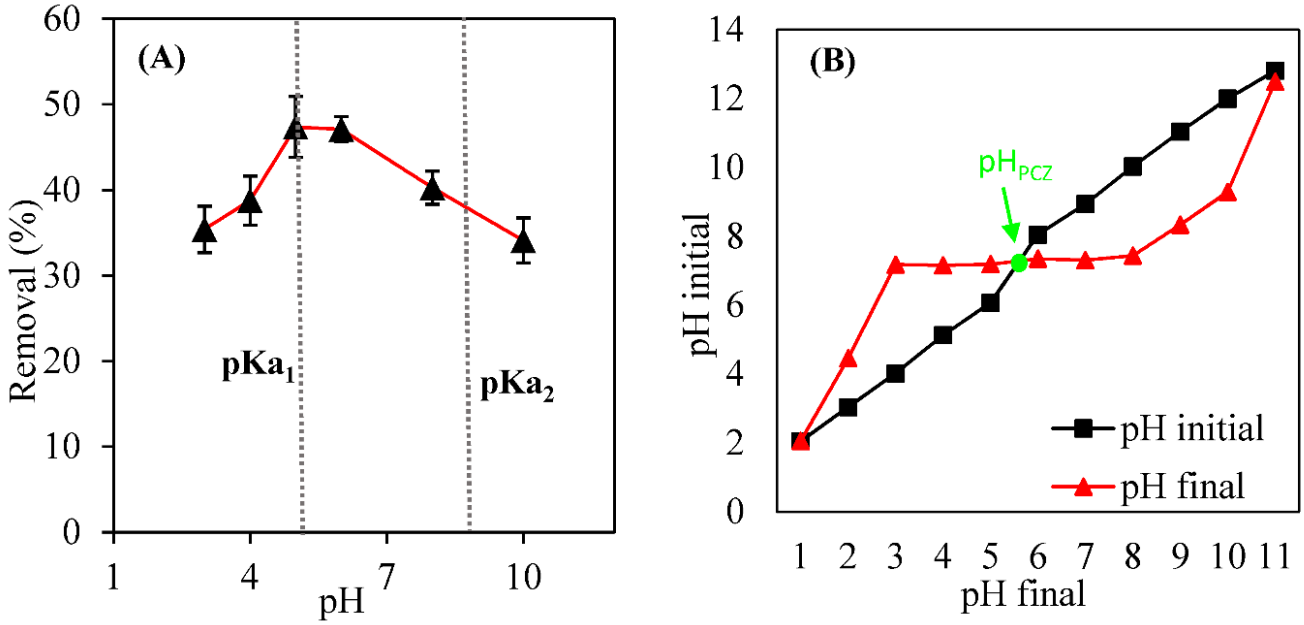

Figure 5. (**A**) Effect of pH on the removal capacity of the CPX and (**B**) the zero charge point pH.

In addition, the role of the biosorbent surface charge was analyzed using the zero charge point pH test (pH_{PCZ}) and different pH ranges (Figure 5b). The pH_{PCZ} of the tested biosorbent was 7.2. A better anion adsorption occurs below this value because the surface of the material is covered by a positive charge; above this value, the adsorbent has a negative charge, which favors the adsorption of cations [20]. The best range of antibiotic removal is in the region the CPX is in the zwitterion form; this is because below a pH 5 and above a pH 8 both CPX and the biosorbent surface will have the same charge, resulting in an electrostatic repulsion [14].

3.4. Biosorption Equilibrium Isotherms

Adsorption isotherms are used for obtaining information regarding the adsorption capacity of a solid, the pore distribution of the material, and some thermodynamic characteristics of the process. The batch adsorption experiments were conducted in the CPX concentration range of 2–10 mg L^{-1}. Figure 6 shows the linear models of Langmuir and Freundlich. Table 3 shows the main parameters calculated for each model.

Table 3. Isotherm model parameters for CPX biosorption by PSB.

Equilibrium Model	Isotherm Parameter	
Langmuir	q_{max} (mg g^{-1})	2.5592
	K_L (L mg^{-1})	1.3747
	R^2	0.9892
	R_L	
Freundlich	K_F (mg g^{-1})	1.4207
	N	3.1184
	R^2	>0.9999

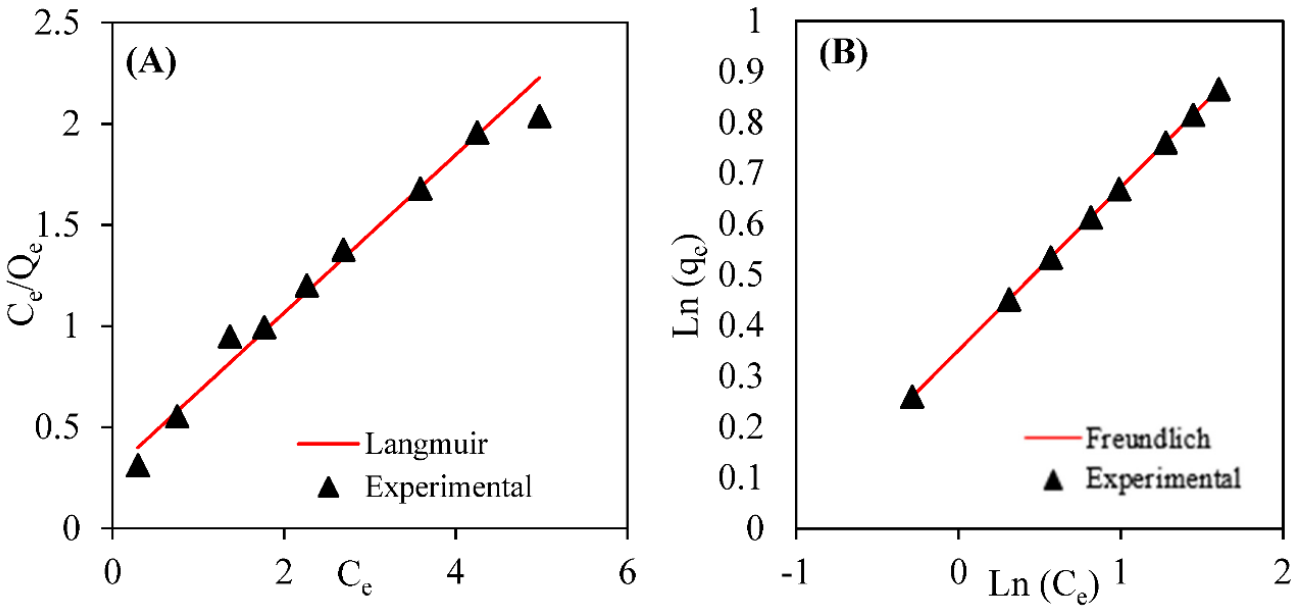

Figure 6. Linear plots of (**A**) Langmuir and (**B**) Freundlich isotherm models for the CPX biosorption by PSB.

The results shown in Table 3 demonstrate, through the coefficients of correlation (R^2), that the Freundlich model best fits the experimental data. The best fit to the Freundlich model suggests that adsorption occurs in multiples layers, and that the adsorbate assumes a heterogeneous distribution on the surface of the solid; this results in a non-uniform energy distribution where there is a variety of interactions between the adsorbate and the adsorbent that correspond to a non-ideal, reversible, and predominantly chemical adsorption [21]. The constant n, correlated to adsorption intensity, reveals how the active sites are distributed in terms of energy capacity. Some authors [5] suggests that for values of n within the range 1 to 10 ($1 < n < 10$), as is the case of CPX adsorption by PSB ($n = 3.1184$), adsorption occurs in a favorable way; this evidences more energetic active sites (cf. non-uniformity of energy distribution) that are previously occupied to the detriment of less occupied ones. Although the Langmuir model did not result in the best experimental fit, it can still be used to obtain some parameters that the Freundlich isotherm does not inform, such as the maximum adsorption capacity; this was at $q_{max} = \pm 2.6$ mg g^{-1}, indicating that the experiment reached the maximum capacity of the adsorbent [10].

3.5. Thermodynamics of Adsorption and Its Modeling

The evaluation of the effects of temperature and thermodynamics provides information about the adsorption mechanism. The adsorption test was performed for different temperatures (10–50 °C). Figure 7A shows the results. Based on the graph, there is a noticeable improvement in the CPX removal process as the temperature rises; this is because at the mildest temperature tested (10 °C) the removal was approximately 26%, while for the high temperature (50 °C), the total removed content was almost 60%. In order to investigate the thermodynamic parameters of the process, the van't Hoff graph (Figure 7B) was plotted; through this graph the variation of Gibbs Free Energy (ΔG), enthalpy (ΔH), and entropy (ΔS) was determined, as Table 4 shows.

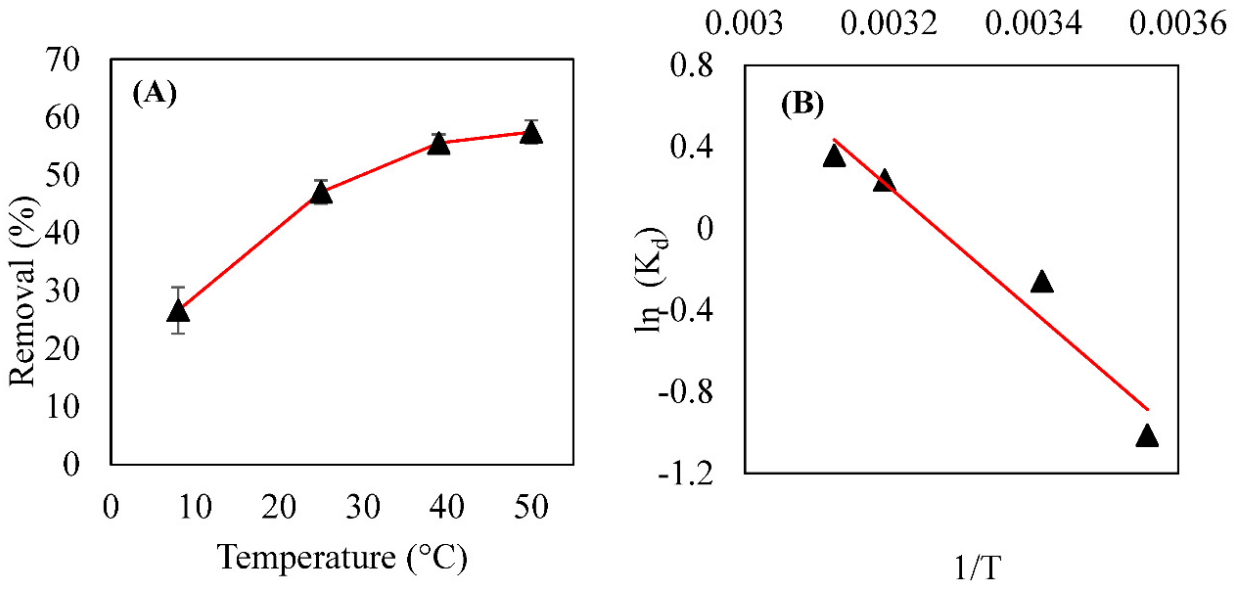

Figure 7. (**A**) Effects of temperature on CPX removal and (**B**) the van't Hoff graph for the system.

Table 4. Thermodynamic parameters of CPX adsorption in PSB.

Temperature (K)	ΔG (J mol^{-1})	ΔS (J mol^{-1})	ΔH (kJ mol^{-1})
281	2366.72	−82.88	25.37
293	628.66		
313	−620.43		
320	−953.84		

The system moves to a minimum of ΔG, which denotes a spontaneity in the process and indicates that the adsorption of CPX by PS develops favorably mainly at higher temperatures. The favoring of this process with the increase in temperature may be due to the dilation of the pores of the adsorbent; this results in larger pores and consequently in an easier diffusion and adsorption of antibiotic molecules [22]. The positive value of ΔH shows an endothermic reaction; this also indicates that adsorption is benefited by the increase in temperature. According to the literature [23], enthalpy values below 20 kJ mol^{-1} denote a physical adsorption nature. On the other hand, for ΔH values greater than 40 kJ mol^{-1}, the predominant interactions in the adsorption process are chemical. As the enthalpy range obtained in the present study remained at an intermediate value (25 kJ mol^{-1}), there is a simultaneous presence of chemisorption and physisorption in the present process; this is the case even though the fitting to the Freundlich isotherm suggests that the process takes place mostly through chemical interactions. The negative value for ΔS shows that there is a reduction in randomness on the solid-liquid interface as the adsorption process is carried out [21,23].

4. Future Perspectives

The present work aimed to propose and adjust a method for the removal of the emerging pollutant Ciprofloxacin via adsorption; it did so by employing the residual biomass resulting from the processing of a pecan nut as an adsorbent. The experiment consisted in determining the characteristics of the residue, and which conditions resulted in higher efficiency for the process. Although the removal efficiency of CPX did not reach the desired maximum (above 90%), the maximum adsorption capacity of the proposed adsorbent (qmax) was 2.5 mg of the CPX per g of PSB. However, since a higher concentration of adsorbate was used, it is possible that when the tested concentrations mimic the real, environmental numbers, a satisfactory process efficiency can be achieved. It is also worth

mentioning that this is an initial research to assess the possible usage of pecan nut shells as an adsorbent; further studies will still be performed with concentration ranges that are closer to those commonly found in the environment.

5. Conclusions

The ability of adsorption of ciprofloxacin by activated charcoal produced from pecan shells was tested under different operational conditions. The batch experiments indicate that the removal of the antibiotic increases with the increase in the contact time with the adsorbent until the system reaches an equilibrium at 240 min. The Freundlich isotherm and the pseudo-second order model result in the best equilibrium and kinetic fitting to the experimental data, respectively. This indicates that adsorption possibly occurs under a strong chemical influence (chemisorption). In addition, the experiments show a strong influence of the medium pH, which may change the charges of the antibiotic molecule and of the PSB surface. Similarly, temperature also exerts an influence on adsorption rates, since the increase in this parameter's values allows achieving higher adsorption rates. The adsorption process is spontaneous and endothermic; therefore, the increase in temperature favors it. Still, the assays reveal that the material used for the production of the adsorbent (pecan shells) after the activation processes can be an alternative treatment for emerging pollutants, in this case antibiotics. This is because it results in high rates of removal of the contaminant associated with the use of waste from the agricultural industry; in turn, this results in the possibility of adding value to an industry by-product that is largely produced in Brazil, generating the possibility of additional income for many local producers, while benefiting the environment.

Author Contributions: Conceptualization L.H. and E.M.E.; methodology, S.G.C.; validation, A.C.W., B.C. and B.R.D.; investigation, D.K.; data curation, V.A.C.; writing—original supervision, L.H.; project administration. All authors have read and agreed to the published version of the manuscript.

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