Highly Effective Adsorption of Caffeine by a Novel Activated Carbon Prepared From Coconut Leaf

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Research Article

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Highly effective adsorption of caffeine by a novel activated carbon prepared from coconut leaf

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Abstract: The disposal of coconut wastes is costly and damaging to the environment, but its uses are advantageous activated carbons production. Coconut leaves waste were used for activated carbon production by pyrolysis at 500°C and activation with potassium carbonate. The activated carbon was used for caffeine removal from aqueous solution. The coconut leaves activated carbon showed a predominantly amorphous structure from X-ray diffraction analysis and a pH at the zero charge point of 7.9. From the N₂ adsorption/desorption method, the adsorbent showed a predominance of mesopores, with average pore size of 45.48 ηm and a
surface area of 678.03 m$^2$/g. From kinetic studies the data followed the pseudo-second order, where the intraparticle diffusion can be neglected. The adsorption isotherms were satisfactorily adjusted for the Redlich-Peterson model and a type curve L was identified. The thermodynamic parameters showed that adsorption occurred spontaneously, was exothermic and governed by physical adsorption. The artificial neural networks developed were capable of predicting both kinetics and equilibrium adsorption data under different operating conditions and was comparable to the traditional models available in literature in the training experiments, encouraging its use for data generalization when an efficient dataset is used. In conclusion, coconut leaves waste showed to be a promising feedstock to produce activated carbon aiming caffeine removal from water and wastewater.

**Keywords:** adsorbent; biochar; carbon; emerging pollutants; kinetic study; surface area
1. Introduction

Coconut is a culture with several uses in people's daily lives and can be processed to obtain a wide variety of value-added products. Coconut grows in more than 97 countries on most continents, Asia, Africa and America[1]. In 2019, the coconut harvested area was 11,807,156 hectares, producing 62,455,08 tons. Indonesia is the world's largest producer of coconut, followed by the Philippines and India. Brazil is the 5th largest coconut producer in the world with 2,330,949 tons [2]. The coconut wastes (shells, leaves and bunches) discarding is both costly and harmful to the environment and its structure, high carbon content and very low ash content are beneficial to synthesize activated carbons [3].

Activated carbons are currently used as an adsorbent in different industries as food, pharmaceutical, chemical, oil, nuclear, automotive and the treatment of water and wastewater [4]. Efficiency and promising operation are the highlight of adsorption technique. This process has great technological maturity and is superior in terms of initial costs, flexibility and simplicity in projects, high efficiency, even at low concentration of pollutants[5,6]. Adsorption methods are already well known, and the literature is full of studies focused on the phenomenological analysis of the process. However, due to the large application of adsorption technology, the search for new and unexplored adsorbents, as well, synthesis routes adsorbents, the precise adjustment of the operating parameters for a low cost preparation, and the effective removal of specific contaminants are still subjects that attract the interest of researchers around the world[7].

In recent years, a new class of contaminants called emerging pollutants (EP) have caused great attention in scientific community. EP are resistant to conventional treatments, toxic and bio-accumulative and they are not comprised in schedules for monitoring water quality and are harmful to the environment and to humans. Their effects and comportment in the environment still demand studies[8,9]. These pollutants are not fully removed in
wastewater treatment units and drinking water stations because of their high complexity, low concentration and the presence of other compounds that can compete or work as inhibitors [9,10].

Thus, several systems have been studied for the removal of EP [11]. Though, adsorption has been attracting the notice of various researchers due to the high efficiency and low cost [12]. Amid emerging pollutants the caffeine is considered a chemical indicator for surface water pollution because its regular consumption [13]. Caffeine is an alkaloid used as a respiratory stimulant, as an additive in medications to increase analgesic effect and also as an appetite regulator. In addition to the natural occurrence of caffeine it can be found in several widely consumed products such as coffee, chocolate, tea, etc. [14].

In the present work, we propose for the first time the production of the activated carbon from the coconut leaves to evaluate its potential for caffeine (CFN) removal from aqueous solution. For this purpose, the activated carbon was obtained by vacuum pyrolysis (500°C) and chemically activated with potassium carbonate (K$_2$CO$_3$). The raw materials were characterized by thermogravimetric analysis (TGA) and the activated carbon by N$_2$ adsorption/desorption analysis, X-ray diffraction (XRD), the pH at the point of zero charge (pH$_{PZC}$). In order to explore the potentiality of the adsorbent to remove caffeine from aqueous solution adsorption kinetic assessments were carried out and the data were evaluated using pseudo-first order, pseudo-second order and intraparticle diffusion models. The effect of temperature was studied in the range 30-50°C and for the better understanding of adsorption phenomenon the Langmuir, Freundlich, Sips and Redlich-Peterson models were fitted to the equilibrium data. The thermodynamics study was conducted to comprehensive the analysis of adsorption mechanism. And to complete the study proposed in this work, artificial neural networks were developed to compare with the conventional models used to foresee kinetic and adsorption equilibrium data.
2 Materials and Methods

2.1 Chemicals

Potassium carbonate (K$_2$CO$_3$, 85%) and caffeine (purity ≥ 99%) were purchased from Sigma-Aldrich. All other chemicals presented analytical grade. CFN has a molecular weight of 194.19 g.mol$^{-1}$ and a pKa of 8.30, which means it is a weak base [15]. Furthermore, CFN has high water solubility (Ks > 10,000 mg.L$^{-1}$), so that hinders its removal in common water and wastewater treatment processes [16].

2.2 Raw material

The coconut leaves (CL) were collected in the city of São Miguel dos Milagres, Alagoas, Brazil, at latitude 9º 14’17.4” South and longitude 35º 21’16.3” West. The leaves were removed at different stages of life. The CL were cut into pieces and dried in an oven (Fanem, Orion 515, São Paulo, Brazil) at 100º C for 24 h [17–19]. The proximate analysis was carried out in triplicate according to the standard methodology from American Society for Testing and Materials (ASTM)-D1762-1984 [20]. The dried sample was analyzed by thermogravimetric (TG) and derivative thermogravimetric (DTG) technique using a thermobalance (TA Instruments, SDT 650, United States). The sample (10 mg) was heated between 27 and 800º C, with a heating rate of 10º C.min$^{-1}$ at an inert atmosphere (N$_2$ gas) with a flow of 40 mL.min$^{-1}$.

2.3 Preparation of activated carbon

Coconut leaves biochar (CLB) were produced by vacuum pyrolysis using a reactor composed of a tubular furnace (JUNG/LT6, 1 kW, 2010) heated by electric resistances. A temperature controller (NOVUS, 1043, Rio Grande do Sul, Brazil) was connected to keep the
temperature at 500°C with a heating rate of 10°C min⁻¹. The system was also composed of 6 condensers responsible for condensing the process gases, collected in three decantation funnels (CB1, CB2 and CB3). A thermostatic bath (Tecnal, TE-184, Brazil) was used to cool the liquid products down to 4°C. A vacuum pump (Fanem, 089/CAL, Brazil) was used to keep a negative pressure of 20 kPa within the system. Pyrolysis experiments were carried out in triplicate using 250 g of CL during a residence time of 2 h [17,20]. Biochar and bio-oil yields were calculated using Equation 1.

\[ Yield_p(\%) = \frac{m_p}{m_i} \times 100 \]  

(1)

where \( m_p \) is the produced mass of biochar and bio-oil (g); \( m_i \) is the initial mass of crude lignin (g); and \( Yield_p \) is the product yield (%). Gas yield was calculated by difference based on the conservation of mass.

CLB samples were chemically activated using anhydrous potassium carbonate (K₂CO₃) at a weight ratio of 1:3 (biochar:K₂CO₃). The mixture was homogenized using distilled water, inserted in a porcelain pot and filled to the reactor under a pressure of 20 kPa and heating rate of 10°C min⁻¹ achieving 600°C for 1 h [18,19]. The system was composed of a stainless steel reactor (height of 20.0 cm, diameter of 20.0 cm and volume of 6.8 L) associated to a vacuum pump (Fanem, 089/CAL, São Paulo, Brazil) and a temperature controller (Novus, N1200, Campinas, Brazil). Steps involved in the activation of the biochar are: biochar maceration, mixture homogenization, activation in the reactor, washing (neutralization) and drying. After the activation, the coconut leaves activated carbon (CLAC) samples were cooled and washed with distilled water to neutralize (pH 7) and to unblock the pores. After, biochar was decanted and separated using a paper filter. Lastly, the sample was dried in the oven (Fanem, Orion 515, São Paulo, Brazil) at 100°C overnight.
2.4 Characterizations

The N\textsubscript{2} adsorption/desorption analysis was conducted at \(-195.91^\circ\) C using a Micromeritics ASAP 2020 equipment. This analysis aimed to determine CLAC textural characteristics such as surface areas and pore diameter. The sample (0.221 g) was pre-treated at 100\(^\circ\) C under vacuum for 12 h. The specific area and the adsorption/desorption isotherms were estimated based on the Brunauer-Emmett-Teller (BET) method until a relative pressure of \(P/P_0 = 0.97\) and by the average pore width in the adsorption. The X-ray diffraction (XRD) and patterns were recorded using a diffractometer (Shimadzu, DRX 6000, Japan), operating with a Cu K\textalpha\ (\(\lambda = 0.1540598\) Å) radiation source in a 2\(\theta\) range of 2–70\(^\circ\) with step of 0.02\(^\circ\). In this case, 0.1 g of the powder sample were analyzed using a voltage of 40 kV and a current of 30 mA. The analysis of pH at the point of zero charge (pH\textsubscript{PZC}) was determined based on the methodology proposed by El-Sayed et al. [21]. In this case, 50 mg of the sample was added in a 50 mL container of solution with the initial pH values ranging from 1 to 12, these values were achieved adding 0.1 mol.L\textsuperscript{-1} of HCl or NaOH. The samples were mixed at 140 rpm, 30\(^\circ\) C for 24 h, after that centrifuged to measure the pH. Finally, inlet and outlet pH values were plotted to obtain the equilibrium pH, which corresponds to the pH\textsubscript{PZC} of the CLAC [16].

2.5 Adsorption study

Kinetic study

The kinetic study, were performed in a finite bath at 27 \(\pm\) 2\(^\circ\) C, with Erlenmeyers (250 mL) were filled with 30 mL of CFN solution, in two different concentrations, 75 and 125 mg.L\textsuperscript{-1}, and 50 mg of activated biochar (d\textsubscript{p} < 0.212 mm). The solutions were kept under constant agitation of 140 rpm (Shaker SL 222 incubator) under time intervals between 2 and 120 min [17]. For each time, the samples were obtained and separated by centrifugation (Solab, SL-700) for 5 min at 3,000 rpm. The concentration of CFN in the sample was obtained by a UV-
vis spectrophotometer (Shimadzu, UV 1800 Spectrophotometer, Japan), at a wavelength of 272 nm [17]. The adsorption capacity \( q_t \) (mg·g\(^{-1}\)) was calculated by Equation 2.

\[
q_t = \frac{(C_0 - C_f)}{M} V
\]  

(2)

where \( C_0 \) is the initial CFN concentration, \( V \) is the solution volume and \( M \) is the mass of adsorbent.

To assess the kinetic comportment, the pseudo-first order [22], the pseudo-second order [23] and Weber-Morris [24] models, presented in Equations 3, 4 and 5, were used to fit the data.

\[
q_t = q_e[1 - \exp(-k_1 * t)]
\]  

(2)

\[
q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t}
\]  

(3)

\[
q_t = k_d t^{0.5} + I
\]  

(4)

where \( q_t \) (mg·g\(^{-1}\)) is the adsorption capacity at \( t \), \( t \) (min) is the time, \( q_e \) (mg·g\(^{-1}\)) is the adsorption capacity at equilibrium, \( k_1 \) (min\(^{-1}\)) is the constant of the pseudo-first order model, \( k_2 \) (g·mg\(^{-1}\).min\(^{-1}\)) is the constant for the pseudo-second order model; \( k_d \) (mg·g\(^{-1}\).min\(^{0.5}\)) is the intraparticle diffusion rate constant and \( C \) (mg·g\(^{-1}\)) signifies the thickness of the boundary layer.

**Equilibrium study**

The equilibrium experiments were carried out in a finite bath system, using 50 mg of activated carbon (\( d_p < 0.212 \) mm) which was placed in a 250 ml conical flask containing 30 ml of CFN solution in concentrations 75, 85, 95, 105, 115, 125, 135 and 145 mg.L\(^{-1}\). The solutions, in duplicate, were left in contact under agitation for 40 min (time defined in the adsorption kinetics experiments) at 140 rpm, 30, 40 and 50º C. After the contact time, the samples were centrifuged for 7 min at 3,000 rpm for separation between adsorbent and aqueous solution. The
CFN final concentration was obtained using a UV-Vis spectrophotometer. The equilibrium data were fitted using the nonlinear models, Langmuir [28], Freundlich [29], Sips [30] and Redlich-Peterson [31], presented in the equations 5, 6, 7 and 8, respectively.

\[
q_e = \frac{q_{max}K_L C_e}{1+K_L C_e} \tag{5}
\]

\[
q_e = K_F C_e^{1/n} \tag{6}
\]

\[
q_e = \frac{q_{max}K_S C_e^{ms}}{1+K_S C_e^{ms}} \tag{7}
\]

\[
q_e = \frac{K_RC_e}{1+a_RC_e^\beta} \tag{8}
\]

where \(q_{max}\) (mg.g\(^{-1}\)) is the adsorption capacity capacity, \(k_L\) (L.mg\(^{-1}\)) is the constant of Langmuir model, \(k_F\) (mg.g\(^{-1}\))(mg.L\(^{-1}\))\(^{-1/n}\) is the constant of Freundlich model, \(1/n\) (-) is the factor of heterogeneity, \(q_S\) is the maximum adsorption capacity for the Sips model (mg.g\(^{-1}\)), \(K_S\) (L.mg\(^{-1}\)) is the constant of Sips model and \(m_S\) (-) is the exponent of the Sips model, \(k_R\) (L.mg\(^{-1}\)), \(a_R\) (L.mg\(^{-1}\))\(^\beta\) and \(\beta\) are constants for Redlich-Peterson.

**Statistical Evaluation**

The quality of models fit was evaluated by the coefficient of determination (R\(^2\)), average relative deviation (ARD), adjusted determination coefficient (R\(^2\)\(_{adjus}\)), and Akaike’s information criterion (AIC) given by equations 9, 10, 11 and 12, respectively.

\[
R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i^{exp} - y_i^{cal})^2}{\sum_{i=1}^{n}(y_i^{exp} - \bar{y}_{exp})^2} \tag{9}
\]

\[
ARD(\%) = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{y_i^{exp} - y_i^{cal}}{y_i^{cal}} \right| \tag{10}
\]

\[
R^2_{adjus} = 1 - \left( \frac{n - 1}{1 - (n_p + 1)} \right) (1 + R^2) \tag{11}
\]
Where $y_i^{exp}$ and $y_i^{calc}$ are the experimental and calculated (model) values from dependent variables $q_i$; $n$ is the number of measured points; and $\bar{y}_i^{exp} = \frac{\sum_{i=1}^{n} y_i^{exp}}{n}$ is used to calculate the mean of the experimental values, $n_p$ is the number of model parameters [32].

**Thermodynamics**

Thermodynamics is an important used tool to understand the influences of temperature on the adsorption mechanisms and their nature. The Gibbs free energy change ($\Delta G^o$), enthalpy change ($\Delta H^o$), and entropy change ($\Delta S^o$) were determined using data from the isotherms and by Equations 13, 14 and 15 [33,34].

\[
\Delta G^o = -RT\ln K_e
\]  
(9)

\[
\Delta G^o = \Delta H^o - T\Delta S^o
\]  
(10)

\[
\ln(K_e) = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}
\]  
(11)

$R$ is the universal constant of gases, $T$ (K) is temperature, $K_e$ is the thermodynamic equilibrium constant, which was determined by the constant of the isotherm model that best fit the experimental data [33,34].

**Ionic Strength and Influence of Aqueous Matrices**

Ionic strength tests were conducted at NaCl concentrations of 0.5;10, 15 and 30% (m/v). The experiments were assessed at 30°C with 75 mg.L$^{-1}$ of caffeine solution in contact with 50 mg of CLAC, at 140 rpm for 40 min of contact. Subsequently, the liquid solution was separated from solids by centrifugation for 7 min at 3,000 rpm. The final concentration of CFN was obtained using a UV-Vis spectrophotometer [35].
With the intention of assess the effect of different aqueous mediums on the caffeine removal, adsorption experiments were achieved using lagoon (Mundaú Lagoon, Maceió/AL, Brazil), tap and mineral water. The initial caffeine concentration was 75 mg.L\(^{-1}\), 50 mg of CLAC, 30° C and 40 min contact time were used for the tests [36].

**Artificial neural networks**

In this work, neural networks were developed to compare their results with the traditional models in the literature used to predict kinetic and adsorption equilibrium data. The purpose of the neural model was also to assess its ability to generalize data. To do so, the adsorption kinetics data for the condition of 125 mg.L\(^{-1}\) and equilibrium data at the temperature of 40 °C were not included in the network database, being used in the network test and validation experiments. The other data referring to the other conditions studied were included in the database and consisted of network training experiments. The metrics used to assess the performance of the network developed and provide its comparison with theoretical models were the coefficient of determination and the average relative deviation.

The feed-forward neural model was used, with the Levenberg-Marquardt technique included into the backpropagation optimization process to calculate the weights and Bayesian regularization to prevent data overfitting. For the neurons in the hidden and output layers, hyperbolic tangent sigmoid and linear activation functions were employed, respectively. To increase the performance of the artificial neural network, the database was first normalized for the training stage, in order to remove any difficulties connected to the varied magnitudes of the data. The data normalization involved setting the rows of each data matrix to 0 and the deviations to 1. Optimization tests were done to establish the network’s ideal structure once the database used for training trials was defined (number of neurons and number of intermediate layers). Thus, starting with the addition of one neuron, the size of the intermediate layer was
changed, and changes in the R2 and ARD were continually monitored. This method was repeated until an optimal number of neurons and hidden layers were found, resulting in excellent output prediction outcomes and, at the same time, physically consistent values to a new pattern that was not addressed in the tests and has yet to be addressed.

3 Results and Discussion

3.1 Raw material characterization

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTG) curves for coconut leaf are presented in Figure 1(a). This analysis is important to obtain information regarding the ideal temperatures for pyrolysis process. The degradation of biomass basically presents three zones. The first zone is up to 200 ºC, it is observed approximately 25% of weight loss. From this point it is observed the degradation of hemicellulose, cellulose and lignin begins. From 150 to 500 ºC is the second zone, with a high mass loss rate, directly linked to the biomass carbonization process. In the third stage, there is a stabilization of the mass loss rate, which also indicates a decrease in the conversion process. Soon after, on the DTG curve, it was possible to observe the presence of two peaks: the first started between 200 and 235 ºC, with a 12% of weight loss of hemicellulose degradation and the second, between 235 and 330 ºC related to the cellulose degradation [37,38]. Lignin is a macromolecule that is difficult to decompose and presents showing a prominent degradation from 330 ºC until the stabilization at approximately 500 ºC. After that, the mass losses were minimized and defining this to be the best point for pyrolysis in order to obtain biochar. This behavior was similar to that described by Almeida et al. [39] who studied coconut fiber pyrolysis and Tsai et al. [40] who pyrolyzed the coconut fiber, sugarcane bagasse and rice husk.
3.2 Pyrolysis yield

Pyrolysis experiments were performed in triplicate, with an initial mass of 250g each. With the results obtained it was possible to calculate the process yield using Equation 2 as shown in Table 1. Bridgwater [41], Goyal et al. [42] and Nayan et al. [43] in their studies defined a typical behavior for the pyrolysis process, 75% of bio-oil and 12% of biochar.

| Product | Yield Run 1 (%) | Yield Run 2 (%) | Yield Run 3 (%) | Average (%) | Standard deviation |
|---------|----------------|----------------|----------------|-------------|--------------------|
| Biochar | 32.44          | 35.68          | 33.84          | 33.99       | 2.29               |
| Bio-oil | 35.32          | 30.44          | 33.00          | 32.92       | 3.45               |
| Gas     | 32.24          | 33.88          | 33.16          | 33.09       | 1.16               |

3.3 Characterizations

Through $N_2$ adsorption/desorption analysis was determined the CLAC surface area of 678.03 $m^2/g$, pore volume of 0.03 $cm^3/g$ and pore diameter of 45.48 nm. Materials with pores between 20 and 50 nm, are classified as mesoporous, thus, the activated carbon of the coconut leaf is within this range [44]. The CFN molecule presents the dimensions 0.78 nm/0.61 nm/0.21 nm, this means that the pore diameter of the biochar, 45.48 nm, is much larger than the dimensions of the CFN molecule, which allows the molecule to access the available active sites inside the pores for adsorption [45]. Regarding the surface area, the value of 678.03 $m^2/g$ is acceptable for the adsorption process when related to the materials used for comparison [46–51]. The $N_2$ adsorption/desorption isotherms are shown in Figure 1(b), they are classified as type IV, characteristic of mesoporous material. The hysteresis also characterizes mesoporous materials and is suitable for the type IV isotherm model. The shape of hysteresis indicates a limitation. Despite easily adsorbing $N_2$, it is not easily release it [32].

The CLAC XRD diffractogram pattern is presented in Figure 1(c) suggesting a typical amorphous characteristic. The diffraction peaks indicate an amorphous material. The broad
peak at $2\theta = 23.32^\circ$ can be related to the typical silica characteristic, and the peak $2\theta = 42.96^\circ$
implies the formation of graphite with a turbostratic structure of amorphous carbon [52–55].
The point of zero charge for the activated carbon was 8.0. Thus, when the activated carbon is
in contact with a liquid solution in which the pH is below $\text{pH}_{\text{pzc}}$, it indicates that this surface is
positively charged. However, when the pH is above $\text{pH}_{\text{pzc}}$, the surface is negatively charged.
The chemical compounds are transformed into cations and anions depending on the pKa and
pH values of the solution [56]. Considering the CFN pKa = 8.3, the adsorption at pH values
close to 8.0 occurs in the neutral form of the CFN molecule, confirmed by the experiments
presented in this work [13].
Figure 1: (a) Thermogravimetric analysis of the coconut leaf; (b) CLAC adsorption/desorption isotherm; and (c) CLAC XRD pattern.
3.4 Adsorption study

Kinetic study

Adsorption kinetic reveals the significant characteristic of adsorption, the transport rate of the adsorbate to the adsorbent surface [57]. The kinetic curves are presented in the Figure 2(a), showing a typical behavior. At the beginning, a high adsorption rate was observed, reaching the equilibrium at 15 min (44.0 mg.g\(^{-1}\)) and 30 min (64.0 mg.g\(^{-1}\)) for 75 and 125 mg.g\(^{-1}\), respectively. Such a behavior, the fast initial adsorption may be associated with the large availability of surface area and active sites. The concentration difference between the solution bulk and the adsorbent surface can act as a driving force to overcome mass transfer barrier. After this initial step, the surface area and sites are gradually blocked and, instead, the adsorption rate decreases. The quantity of desorbing adsorbate on the adsorbent surface and the amount of adsorbent adsorbate on the surface are in dynamic equilibrium at this moment. Another issue to be addressed is that at higher concentrations the adsorption capacity is higher. This is because at high concentrations there are more molecules occupying the available active sites [57–60].

In order to understand the dynamics of interactions between caffeine and activated carbon, the kinetic models of pseudo-first order (PFO), pseudo-second order (PSO) and intraparticle diffusion were adjusted to the experimental data and the parameters are presented in Table 2. The higher coefficients of determination (R\(^2\) > 0.89) and lower average relative deviation showed a better fit of the experimental data to the pseudo-second order model. Despite the fact that neither PFO and PSO models describe the adsorption mechanism, the difference between the mean solid phase concentration and the equilibrium concentration is assumed to represent the driving factor for adsorption by both models. In this case, the
adsorption rate for the PFO model would be proportional to the driving force, while for the PSO model, it would be proportional to the square of the driving force [61–63].

Figure 2(b) show the adjustment of the experimental data to the intraparticle diffusion model. When plotting $q_t$ as a function of $t^{0.5}$, the intraparticle diffusion step will govern adsorption if the resulting curve is linear and passes through the origin. If two phases can be distinguished, the first curve represents diffusion in the particle's outer layer, while the second curve represents diffusion in the particle's inner layer. As a result, the two stages of external diffusion and intraparticle diffusion regulate caffeine adsorption by coconut leaves activated carbon (CLAC) [27,35,64].

**Equilibrium study**

In order to comprehend the mechanism of interaction amid the caffeine molecules and the coconut leaves activated carbon the adsorption isotherms were obtained, shown in Figure 2 (c-e). Giles et al. [65] describes a classification of solid-liquid isotherm and suggests that its shape can be used to define the adsorption mechanism, physical nature of the solute, substrate surface and specific product surface area. Thus, the obtained isotherms can be considered type L2, that presents an initial curvature facing downwards, indicating a reduction in the availability of active sites with the increase of adsorbate concentration. As more places in the adsorbent surface are occupied, it becomes more difficult for the CFN molecules to find an empty spot. The plateaus suggest that all available locations on the original adsorbent surface were filled [34,59].

To better understand the adsorption mechanism, non-linear isothermal models were used to fit the experimental data. Therefore, four models were tested: Langmuir, Freundlich, Redlich-Peterson and Sips. The results are presented in Table 2. Considering $R^2$ values, all models have values above 0.98, which makes this criterion not decisive. The second statistical
criterion analyzed was the $R^2_{adj}$, where the best values were for the Redlich-Peterson and Sips models. The smallest ARE values was obtained for the Redlich-Peterson model. However, according to the AIC criterion, the lowest values was for the Freundlich model. Yet, the Redlich-Peterson model has components of the Langmuir and Freundlich equations. For the constant $\beta$ values close to 1 the Redlich-Peterson model presents Freundlich characteristics, and for $\beta$ values close to 0 it presents Langmuir characteristics, so in the Redlich-Peterson model can represent the equilibrium data caffeine adsorption onto coconut leaves activated carbon.

Finally, Table 3 compares the adsorption performances of alternative adsorbents in order to cover the adsorbent's future applicability to various contaminants. It can be noted that the adsorption capacity findings obtained are on the same order of magnitude as those obtained in the current work, checking the positive result achieved.
Figure 2: (a) Kinetic curves; (b) Weber-Morris intraparticle diffusion model and adsorption isotherms at (c) 30 °C, (d) 40 °C and (e) 50 °C.
**Table 2:** Kinetic, equilibrium and thermodynamic parameters for CFN adsorption using CLAC

| Kinetic Parameters | 75 mg.L\(^{-1}\) | 125 mg.L\(^{-1}\) |
|-------------------|------------------|------------------|
| **Pseudo-First Order** | | |
| R\(^2\)           | 0.744            | 0.644            |
| q\(_e\) (mg.g\(^{-1}\)) | 43.68            | 59.53            |
| ARD (%)           | 0.203            | 3.73             |
| k\(_1\) (min\(^{-1}\)) | 0.9657           | 0.7843           |
| **Pseudo-Second Order** | | |
| R\(^2\)           | 0.963            | 0.893            |
| q\(_e\) (mg.g\(^{-1}\)) | 45.01            | 63.69            |
| ARD (%)           | 0.87             | 2.45             |
| k\(_2\) (min\(^{-1}\)) | 0.0537           | 0.0240           |

| Equilibrium Model | Parameter | 30°C | 40°C | 50°C |
|-------------------|-----------|------|------|------|
| **Langmuir**      | q\(_{exp(max)}\) (mg/g) | 73.83 | 69.79 | 72.94 |
|                   | q\(_{calc(max)}\) (mg/g) | 73.13 | 70.51 | 71.39 |
|                   | K\(_L\) (L/mg) | 1.343 | 0.987 | 1.393 |
|                   | R\(^2\) | 0.980 | 0.989 | 0.976 |
|                   | R\(^2\)\(_ajustado\) | 0.40 | 0.40 | 0.40 |
|                   | ARD | 3.96 | 2.99 | 4.83 |
|                   | AIC | 22.97 | 18.72 | 24.85 |
| **Freundlich**    | n | 5.89 | 7.56 | 6.54 |
|                   | K\(_F\) [(mg/L)(L/g)\(^{1/n}\)] | 43.55 | 46.66 | 45.87 |
|                   | R\(^2\) | 0.989 | 0.987 | 0.994 |
|                   | R\(^2\)\(_ajustado\) | 0.40 | 0.40 | 0.40 |
|                   | ARD | 3.61 | 3.09 | 1.95 |
|                   | AIC | 19.66 | 19.10 | 13.02 |
| **Redlich-Peterson** | K\(_R\) (L/mg) | 292.00 | 149.76 | 599.29 |
|                   | a (L/mg)\(^{\beta}\) | 12.75 | 2.52 | 12.39 |
|                   | B | 0.847 | 0.943 | 0.867 |
|                   | R\(^2\) | 0.989 | 0.992 | 0.998 |
|                   | R\(^2\)\(_ajustado\) | 0.75 | 0.75 | 0.75 |
|                   | ARD | 3.61 | 2.83 | 1.92 |
|                   | AIC | 25.16 | 21.96 | 18.05 |
| **Sips**          | q\(_{max}\) (mg/g) | 158.99 | 78.22 | 115.39 |
|                   | K\(_s\) (L/mg) | 0.367 | 1.235 | 0.633 |
|                   | m\(_S\) | 0.271 | 0.594 | 0.322 |
|                   | R\(^2\) | 0.989 | 0.992 | 0.996 |
|                   | R\(^2\)\(_ajustado\) | 0.75 | 0.75 | 0.75 |
|                   | ARD | 3.77 | 2.82 | 1.90 |
|                   | AIC | 25.26 | 22.08 | 16.89 |

| Thermodynamics   | ΔG\(^o\) (kJ.mol\(^{-1}\)) | -49.10 | -48.99 | -54.28 |
|                  | ΔH\(^o\) (kJ.mol\(^{-1}\)) | -28.35 | -28.35 | -28.35 |
|                  | ΔS\(^o\) (kJ.mol\(^{-1}\)) | 0.253 | 0.253 | 0.253 |
Table 3: Comparison of some adsorbents for caffeine adsorption

| Adsorbent                                           | $q_{\text{max}}$ (mg/g) | Conditions          | Reference |
|-----------------------------------------------------|--------------------------|---------------------|-----------|
| Combined powder and granulated activated carbon    | 12.63                    | 24 h, 20 °C         | [66]      |
| Synthetic xerogel coals                            | 182.5                    | 48 h, 30 °C         | [67]      |
| Oxidized carbon derived from *Luffa cylindrica*     | 59.88                    | 24 h, 25 °C         | [68]      |
| Pine needle biochar                                 | 6.54                     | 150 min, 40 °C      | [69]      |
| Activated pineapple leaf biochar                    | 155.5                    | 4 h, 25-55 °C       | [70]      |
| Fique bagasse biochar                              | 19.55                    | 16 h, 25 °C         | [71]      |
| Commercial multi-walled carbon nanotubes           | 4.18                     | 2 h, 25 °C          | [72]      |
| Commercial granulated activated carbon             | 88.00                    | 2 h, 25 °C          | [72]      |
| MgAl-LDH / Bovine bone biochar                     | 26.219                   | 30 min, 40 °C       | [14]      |
| Fixed bed activated carbon                         | 270.0                    | 3 days, 30 °C       | [73]      |
| Sepiolite clay                                     | 48.7                     | 12h, 25 °C          | [74]      |
| Coconut leaf activated carbon                      | 73.83                    | 40 min, 30 °C       | This work |

**Thermodynamic study**

Using the equilibrium data obtained at 30, 40 and 50 °C it was possible to determine the thermodynamic parameters, Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) using the procedure presented by Piccin et al [34]. The free energy values of Gibbs ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) are showed in Table 2. The negative values of $\Delta G^\circ$ determine that the adsorption is spontaneous and favorable. In addition, the positive $\Delta S^\circ$ value indicates that there was a change in the structure of the adsorbent and an increase in randomness during CFN fixation in active sites. $\Delta H^\circ$ negative value indicate the adsorption is exothermic. The negative and low $\Delta H^\circ$ values indicate the weak adsorption forces and physical and exothermic nature[12,75–77].

**Ionic Strength and Influence of Aqueous Matrices**
The effect of ionic strength on the adsorption of caffeine onto coconut leaf activated carbon is depicted in Figure 3(a). Despite changing the ionic strength of the solution, the adsorption capacity of the CLAC remained nearly constant, according to the experimental results. As a result, electrostatic interactions have no effect on the adsorption of caffeine onto CLAC.

The use of coconut leaf activated carbon for caffeine removal from real matrices is an important complementary step in this study. The collected data of this step is presented in Figure 3(b). The removal was 44.7, 40.8 and 65.9 % for lagoon, tap and mineral water, respectively. The delineated results endorse the validity and applicability of CLAC for caffeine removal in different water mediums.

![Effect of ionic strength](image-a)

![Effect of aqueous matrices](image-b)

**Figure 3**: (a) Effect of ionic strength; (b) effect of aqueous matrices

### 3.6 Artificial neural networks

The results of the neural network predictions for the adsorption kinetic data and equilibrium isotherms are presented in Figures 5 and 6, respectively. As it can be seen in the results presented, the developed neural network was adequate to predict the kinetics adsorption data, but it had difficulty in predicting the adsorption equilibrium data for values of $C_e$ lower than 5 mg.L$^{-1}$ for the data not used in the training step (Figure 6.b), but there is room for improvement of the network. It must be taken into account, however, that $C_e$ values are
different for each temperature condition tested, that is, the amount adsorbed at equilibrium is
dependent on the concentration values for each temperature condition. As a neural model is a
model that interpolates values, the global adjustment is compromised, given the network's
difficulty in structuring its learning in the face of the non-uniformity of the independent
variable's data.
**Figure 5**: Observed and predicted equilibrium data by the neural model developed in this work. The condition $q_t = 125$ mg.L$^{-1}$ (red color) corresponds to the ANN testing experiments.

**Figure 6**: Observed and predicted equilibrium data by the neural model developed in this work: (a) training experiments for the condition of 30° C; (b) testing experiments for the condition of 40° C; (c) training experiments for the condition of 50° C.
As presented in Figure 5, this was not observed for the results referring to the adsorption kinetics, in which, for the same time interval, the network performance was satisfactory, even considering only the adsorption kinetic data for the dataset of the 125 mg.L\(^{-1}\) condition. These results do not detract from the neural network, which, in addition to presenting a good performance for adsorption kinetics, proved to be an excellent tool to predict equilibrium data for the other analyzed temperature conditions used in its database (figures 6 a and c). In fact, with a more efficient database, the neural network could be more accurate. Even so, for data not used in the training step, the \(\text{ARD}\) value was below 5\%, encouraging its use for future studies on the optimization of effluent adsorption processes using the solid waste of an organic nature, both regarding kinetics and isotherms of adsorption.

It is worth mentioning that the developed neural network presented a very simple structure and low computational cost, with no tendencies towards the overfitting problem. The resulting mathematical model is simple and can be used with good accuracy to predict caffeine adsorption data using coconut leaf residues within the range of operating conditions studied. The coefficient of determination was greater than 0.99 for the training experiments and equal to the unity for the kinetic experiments. Little data was used in the training of the network, which reinforces its good performance. The \(\text{ARD}\) value was below 5\% in all the cases analyzed, showing a very little deviation from the experimental values.

In comparison with the classical models presented in the literature, such as the Langmuir, Freundlich, Redlich-Peterson, and Sips models, the accuracy of the neural network was comparable to these models in predicting the data used in the training experiments. It should be noted that these models do not have the ability for data generalization. Similar results were also found for the adsorption kinetics experiments.

4. Conclusion
From the results obtained in this study, the coconut leaf activated carbon achieved good results of caffeine adsorption reaching a maximum theoretical adsorption capacity of 73.83 mg.g\(^{-1}\) at 30\(^\circ\) C in 40 min of adsorption. The pseudo-second order model adequately described the kinetic data and the Redlich-Peterson model well fitted the equilibrium isotherms. The adsorption was exothermic, spontaneous and favorable. It was determined a change in the structure of the adsorbent and an increase in the randomness during CFN fixation in active sites. The ionic strength of the solution has no effect on the adsorption of caffeine onto CLAC. The studied adsorbent demonstrated be suitable for caffeine removal in different water mediums. The artificial neural networks developed in this work were capable of predicting both kinetics and equilibrium adsorption data under different operating conditions. Even for data not used in the network database in the training experiments, the highest mean absolute percentage error obtained was less than 5%, showing that the neural model can be considered an interesting tool for future studies on optimization of adsorption processes and data generalization. The neural model also proved to be comparable to the traditional theoretical models presented in the literature for predicting isotherm and adsorption kinetics data. Finally, the coconut leaf activated carbon, unexplored for this use, appears to be an exceptional alternative adsorbent, as it is an abundant biomass available at low cost.

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