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Hydrothermal carbonization of coffee husk: Optimization of experimental parameters and adsorption of methylene blue dye


Laboratory of Environmental and Agrochemistry, Department of Chemistry, The State University of Maringá, Av. Colombo 5790, CEP 87020-900, Maringá, Paraná, Brazil.

*Corresponding author: Tel: + 55 44 3011 4500; fax: + 55 44 3011 4449

Email address: vcalmeida@uem.br (V.C. Almeida)

Graphical Abstract

Highlights

- Coffee husk was used as precursor of hydrochar.
- The experimental parameters were successfully optimized from RSM.
- Temperature and time were the significant effects.
- The optimized hydrochar (HC_{op}) exhibited well-developed surface area.
- HC_{op} showed monolayer adsorption capacity of 34.85 mg g^{-1} for MB.

Abstract

The coffee husk was used as precursor of hydrochar and chemometrics tools were applied to optimize
the experimental conditions in order to obtain hydrochar with well-development surface area. The central composite rotatable design was employed and the optimization of parameters (temperature, time and water:precursor ratio) was performed from Response Surface Methodology (RSM). The analysis of variance showed that significant effects were: temperature and time. The optimal condition was found to be: temperature of 210 °C, time of 243 min, and water:precursor ratio of (3.4:1), resulting in a hydrochar (HCop) with BET surface area value ($S_{\text{BET}}$) of 31.3 m$^2$ g$^{-1}$. The HCop was properly characterized and applied in adsorption studies of Methylene Blue (MB) dye. The adsorption studies showed that the Elovich kinetic model and Langmuir isotherm model were that better described the experimental data. The monolayer adsorption maximum capacity of HCop was estimated to be 34.85 mg g$^{-1}$. Additionally, the thermodynamic study showed that adsorption occurs via spontaneous and endothermic process.

**Keywords:** Hydrochar; coffee husk; hydrothermal carbonization; response surface methodology; adsorption.

**1. Introduction**

Carbonaceous materials with well-developed surface areas have been used in adsorption processes for removal of organic and inorganic pollutants. The efficiency of adsorption is due the textural properties and functional groups present on the materials' surfaces. On the other hand, the main disadvantage is associated to the high production costs, which has motivated several researchers to study new routes and methodologies of synthesis. In this regards, the hydrothermal carbonization (HCT) emerges as a viable and efficient alternative for preparation of carbonaceous materials (hydrochar) that can be applied as adsorbent materials [1].

HCT consists of the suspension of raw material (precursor) in water followed by heating in a high pressure system [2]. During the process, the subcritical water reacts with lignocellulosic biomass polymers, which are cleaved in lower molecular weight structures through simultaneous reactions, such as hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization [3]. The HCT process presents some advantages, when compared to others methodologies for
synthesis of carbonaceous materials, such as low environmental impact (use of water as solvent); by-products as hydrochars precursors (biomass) and low energy consumption [4]. Besides the HCT is an inexpensive and clear procedure, different materials have been used as precursors for production of hydrochars, such as: food residues [5], switchgrass [6], corn stalk [7], eucalyptus bark [8], poultry litter [9] and bamboo [1]. The hydrochars have been applied in different processes, including energy production, agriculture, carbon sequestration, bio-refinery, etc [3]. However, the adsorption of heavy metals, nutrients, aromatic compounds, pesticides and herbicides from aqueous solutions has also recently been reported as the most promising application of hydrochars, since they are low cost rich carbon materials commonly derived from abundant and renewable feedstock sources, [1,5,6].

The physicochemical properties of hydrochars are directly related with the precursor and experimental conditions used in the HCT (temperature, time and water:precursor ratio) [3,10]. Therefore, an efficient control of synthesis parameters allows to obtain hydrochars with desired characteristics from milder conditions. In this regard, multivariate statistical techniques are valuable tools for optimization of these experimental parameters.

The Response Surface Methodology (RSM) is one of the most used multivariate techniques for optimization of processes. The experimental design allows to study the adequate conditions for preparation (e.g. hydrochar), in order to obtain materials with lower production costs and adequate responses with statistical accuracy [11,12]. From the fitting of a polynomial model to the experimental data, it is possible to predict the response for all possible combinations of factors within the chosen experimental group [13]. Thus, it is possible to define which parameters are most important for the preparation of materials, such as hydrochar.

Coffee is the most consumed drink around the world, being usually served hot, however, it is also consumed cold. The coffee processing can be carried out using the damp or dry process. Dry process consists of removal of husk and pulp from the grain, corresponding to 45% of total mass of fruit, and which are main waste of coffee's industries. Coffee husk represents 12% of dry mass of fruit and it is constituted mainly of cellulose, hemicellulose and lignin [14]. Therefore, several works
have proposed the use of coffee husks as precursor of biosorbent [15] and activated carbons [16]. However, to the best of our knowledge, there are not works in the literature which propose the use of coffee husk as precursor of hydrochars and that employed the RSM for the optimization of experimental parameters.

The aims of present work were to prepare hydrochar from coffee husk and optimize the experimental parameters using the RSM for obtaining a hydrochar with larger surface area. The parameters investigated on surface area development of the hydrochar from HCT treatment were as following: temperature, time and water:precursor ratio. The raw material and optimized hydrochar (HC_{op}) were characterized from N2 adsorption/desorption isotherms, contents of inorganic elements, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and pH in the point of zero charge (pH_{PZC}), with purpose of investigating the modifications promoted by the HCT from the raw material. The HC_{op} was applied in the adsorption of methylene blue (MB) dye. The MB is a cationic dye with wide industrial application, and which has been used as model dye in adsorption studies.

2. Materials and methods

2.1. Precursor and proximate analysis

The coffee husks were provided by a coffee processing plant located in Maringá City, Paraná State, Brazil. Firstly, the material was washed with portions of distilled water for removal of impurities, and dried in oven at 60 °C for 24 h. Then, the precursor was ground and stored for further analysis. Proximate analysis (moisture, ash, volatile materials and fixed carbon) was carried out according to standard method ASTM-D1762-84 [17], using a muffle furnace (EDG equipment, EDG3P-S 7000).

2.2. Hydrochar preparation

HCT was carried out in autoclaves consisting of stainless steel reactors and Teflon® containers of total volume of 75.0 mL. Amounts of 8.000 g of precursor were mixed with different volumes of distilled water in Teflon® containers and inserted into the stainless-steel reactors. The autoclaves were
submitted to different temperatures and times, using a muffle furnace with heating rate of 20 °C min⁻¹. After cooling, the materials were washed several times with distilled water and dried at 60 °C for 24 h. The yield for each hydrochar synthesized was calculated from relation shown in Eq. 1:

\[
\text{Yield(%) } = \frac{W_c}{W_0} \times 100
\]  

(1)

where \( W_c \) and \( W_0 \) are the final and initial weight values (g).

2.3. Experimental design

The experimental design was performed from the central composite rotatable design (CCRD). The investigated factors were temperature \((x_1)\), time \((x_2)\) and water:precursor ratio \((x_3)\). The codified and real levels used for obtaining the experimental design are shown in Table 1. The real level values were selected taking into account studies reported in the literature. The codified values in superior and inferior levels were calculated from Eq. 2:

\[
x_i = \frac{x_i - X_0}{\Delta X_i}
\]  

(2)

where \( x_i \) is the codified value for each variable, \( X_i \) is the real value, \( X_0 \) is the value for each factor at central point, and \( \Delta X_i \) is the difference between the levels for each factor. The codified values for axial points were calculated from Eq. 3:

\[
\alpha = \frac{4}{n_{fat}^{1/4}}
\]  

(3)

where \( \alpha \) is the axial point and \( n_{fat} \) is the number of experiments of the factorial design \( 2^3 \). The experimental data were adjusted to a second-order polynomial regression model, according to Eq. 4:

\[
y_i = \beta_0 + \sum_{i=1}^{k} \beta_i x_i^1 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon
\]  

(4)

where \( y_i \) is the response, \( \beta_0, \beta_i, \beta_{ii}, \beta_{ij} \) are the regression coefficients (\( \beta_0 \) is the average of response, \( \beta_i \) is the linear term, \( \beta_{ii} \) is the quadratic term and \( \beta_{ij} \) is the term related with interaction effects) and \( \varepsilon \) is the residual associated to the experiments.

Table 1

The selected response for model evaluation was the natural logarithm of BET surface area.
value ($ln S_{BET}$). The analysis of variance (ANOVA) was performed from the Design-Expert® 7.1.3 software (Stat-Ease Inc., Minneapolis, MN). The Response Surface Methodology (RSM) and Desirability Function ($d$) were used to optimize the preparation parameters in order to obtain a hydrochar with large surface area.

2.4. Characterization of materials

$N_2$ adsorption-desorption isotherms at 77 K were obtained from QuantaChrome® Nova 1200e surface area analyzer. The surface area was calculated through linear fit of Brunauer-Emmett-Teller (BET) equation to relative pressure range ($p/p^o$) of 0.05-0.20. Total pore volume ($V_t$) was defined as the maximum $N_2$ amount adsorbed at relative pressure $p/p^o = 0.99$, and the micropore volume ($V_µ$) was calculated from deBoer method [18]. The average pore diameter ($D_p$) was estimated by the relation $4V_µ/S_{BET}$ and pore size distribution was calculated from Non-local Density Functional Theory (NLDFT) [19].

The macro and micronutrients analyses were carried out from digestion of raw material and $HC_{op}$ with nitropercloric solution. The contents of s of Mg, Ca, K, Fe, Cu, Mn and Zn were determined by flame atomic absorption spectrometry (F AAS) using a PerkinElmer AAnalyst 200 Spectrometer with air-acetylene flame, whereas P, S and B contents were determined by UV-Vis spectroscopy (Agilent, Cary 60). The total N was determined from Kjeldahl classic method [20].

FT-IR spectra were recorded from a Thermo Scientific Nicole IZ10 spectrometer. The data were registered with resolution of 4 cm$^{-1}$ and acquisition rate of 20 scans min$^{-1}$ with wavenumber ranging from 400 to 4000 cm$^{-1}$. The pellets for analysis were obtained by soaking KBr with 1% of samples (raw material and $HC_{op}$) in an agate mortar. The morphology of raw material and $HC_{op}$ were investigated from SEM images using a scanning electron microscope (Shimadzu SS 550). Thermal stability of the raw material and $HC_{op}$ was investigated from thermogravimetric analysis (TGA), which was carried out by a thermogravimetric analyzer (Netzsch® Germany STA 409), under $N_2$ flow of 100 mL min$^{-1}$ and heating rate of 10 °C min$^{-1}$ from the room temperature ($≈30$ °C) until 800 °C. The pH in the point of zero charge ($pH_{PZC}$) of $HC_{op}$ was determined from the methodology reported.
by Prahas et al. [21].

2.5. Bath adsorption studies of methylene blue (MB)

2.5.1. Effect of pH

The evaluation of pH effect on the MB adsorption was performed using solutions with initial concentration of 300 mg L\(^{-1}\). The pH values of solutions were adjusted in the range of 3.0 to 10.0, using HCl (0.10 mol L\(^{-1}\)) and NaOH (0.10 mol L\(^{-1}\)) solutions. Aliquots of 25.0 mL of the solutions were placed in contact with 0.125 g of HC\(_{op}\) and shaken for 240 min at 220 rpm (30 °C). Then, the solutions were centrifuged and the remaining MB concentrations determined by an UV-Vis spectrophotometer (Agilent, Cary 60) at the maximum wavelength (\(\lambda\)) of 664 nm, employing a calibration curve. The MB adsorbed amounts on HC\(_{op}\) for each initial pH value of the solutions (\(q\_e; \text{mg g}^{-1}\)) were calculated from Eq. 5.

\[
q\_e = \frac{(C_0 - C_f)V}{m}
\]  

(5)

where, \(C_0\) and \(C_f\) is the initial and final concentration of MB (mg L\(^{-1}\)), \(V\) is the volume (L) and \(m\) is the mass of HC\(_{op}\) (g).

2.5.2. Adsorption kinetics

Kinetic studies were carried out using 25.0 mL of MB solution with initial concentrations of 100, 300 and 500 mg L\(^{-1}\) (pH = 5.5) and 0.125 g of HC\(_{op}\), which were placed into polypropylene flasks and shaken by 2.5 to 240 min at 220 rpm (30 °C). After shaking, the solutions were centrifuged and MB remaining concentrations determined from the spectrophotometric measurements. The adsorbed amount of MB onto HC\(_{op}\) at time \(t\) (\(q\_t\)) was calculated by Eq. 6.

\[
q\_t = \frac{(C_0 - C_t)V}{m}
\]  

(6)
where, $C_0$ is the initial concentration (mg L$^{-1}$), and $C_t$ is the concentration at time $t$ (mg L$^{-1}$), $V$ is volume (L) and $m$ is the mass of HC$_{op}$ (g).

2.5.3. Adsorption equilibrium and thermodynamic

Adsorption equilibrium studies were performed using 25.0 mL of MB solution with initial concentrations ranging from 25 to 500 mg L$^{-1}$ (pH = 5.5) and 0.125 g of HC$_{op}$, which were placed into polypropylene tubes and shaken for 240 min (30 ºC and 220 rpm). Then, the solutions were centrifuged and MB remaining concentrations were determined by spectrophotometry. The MB adsorbed amounts onto HC$_{op}$ at the equilibrium ($q_e$, mg g$^{-1}$) were determined from Eq. 5.

The effect of temperature in the adsorption of MB onto HC$_{op}$ was evaluated using 0.125 g of adsorbent and 25.0 mL of 500 mg L$^{-1}$ MB solution (pH = 5.5), which was shaken for 240 min (220 rpm) at temperatures of 30, 40 and 50 ºC. The maximum amount of MB adsorbed on HC$_{op}$ at each temperature was calculated from Eq. 5, and the thermodynamic parameters determined by equations listed in Table S1 (Supplementary Information section), using the dimensionless $K_C$ constant [22]. All experiments were carried out in duplicate.

2.5.4. Adsorption isotherm and kinetic models

The equations of isotherm and kinetic models evaluated are shown in Table S1. The pseudo-first order [23], pseudo-second order models [24] and intra-particle diffusion model [25] were fitted to the kinetic data, , while Langmuir [26], Freundlich [27] and Dubinin-Radushkevich [28] models were fitted to the equilibrium adsorption data. All models were fitted to the experimental data using the Origin 6.1® software. The fits of the theoretical models were evaluated from the values of determination coefficients ($R^2$) and normalized standard deviation values ($\Delta q_e$) [29]. The $\Delta q_e$ (%) was calculated from Eq. 7.

$$\Delta q_e = 100 \sqrt[2]{\frac{\sum (q_{e,\text{exp}} - q_{e,\text{cal}})^2}{N-1}}$$  \hspace{1cm} (7)
where, $q_{e,\text{exp}}$ is the experimental adsorption capacity, $q_{e,\text{cal}}$ is the calculated adsorption capacity, and $N$ is the number of data points.

3. Results and discussion

3.1. Proximate analysis of raw material

The proximate analysis results of raw material were found to be 7.3, 76.1, 4.9 and 19.0% for the moisture, volatile materials, ash and fixed carbon (from the dry mass), respectively. These results indicate that the coffee husk can be employed as precursor of hydrochars, once exhibits low ash content and substantial amount of fixed carbon. Similar results for coffee husk were reported by Rambo et al. [30].

3.2. Experimental design and yields

The experimental design with real and codified values of factors, surface area ($S_{\text{BET}}$), values of the fitted response ($y_1 = \ln S_{\text{BET}}$) and hydrochar yields are shown in Table 2. The CCRD design with 3 factors and 5 levels was constituted by 18 experiments; 8 corresponding to $2^3$ complete factorial design, 6 axial points and 4 replicates in the central point.

Table 2

As can be seen in Table 2, the highest values of response ($y_1$) corresponded to the highest $S_{\text{BET}}$ values. The $S_{\text{BET}}$ values of hydrochars ranged from 2.05 to 31.22 m$^2$ g$^{-1}$, indicating a significant development of porosity from the hydrothermal procedures performed. Additionally, it is possible to observe that yields of hydrochars are influenced by investigated parameters, once the highest yield value was observed for lowest carbonization time, while the lowest value was found for the highest carbonization time. The yields of hydrochars ranged from 52.52 to 63.70%. Nizamuddin et al. [31]
reported that high values of time and temperature of carbonization promote a decrease in yield values.

3.3. Model fitting and analysis of variance (ANOVA)

The analysis of variance (ANOVA) was applied to evaluate the significant factors and the model fit. Statistical analysis of factors was performed through hypothesis test ($p$-value) and $F$-test. A factor or interaction between factors will be significant if the value of calculated $F$ ($F_{cal}$) is higher than that tabulated value ($F_{tab}$) for the respective degrees of freedom. Besides, $p$-value must be in an interval which satisfies the relation $p \leq \alpha$ for the respective degrees of freedom. Considering a confidence interval of 95%, factors or interactions that exhibit $p \leq 0.05$ are significant and the null hypothesis can be rejected. Table S2 (Supplementary Information) shows the analysis of variance (ANOVA) for the factors: temperature ($x_1$), time ($x_2$) and water:precursor ratio ($x_3$). According to the data (Table S2), the significant factors were: the linear terms $x_1$ and $x_2$, and the quadratic term $x_2^2$, which showed $p$-values lower than 0.05. The quadratic regression model fitted to the response ($\ln S_{BET}$) in terms of coded factors and excluding non-significant factors is described by Eq. 8.

$$\ln S_{BET} = 2.67 + 0.710x_1 + 0.460x_2 - 0.26x_2^2$$

(8)

The positive coefficients of $x_1$ and $x_2$, shown in Eq. 8, indicate that an increase in their values promote an increase on the response ($y_1 = \ln S_{BET}$), and consequently on $S_{BET}$ value. On the other hand, negative coefficient of quadratic term ($x_2^2$) indicates that an increase in the time causes a decrease in the response. The increase of surface area occurs due to removal of oxygenated volatile compounds from the precursor structure, converting it to hydrochar [32]. Additionally, at temperatures above 190 °C occur hydrothermal destruction of cellulose, whereas at temperatures higher than 230 °C result in an accelerated degradation of the material [33].

The analysis of variance for the quadratic regression model fitted to the response $y_1$ is shown in Table S3. It is possible to observe that the calculated $F$-value for the quadratic model was 16.38, which is higher than that tabulated value for respective degrees of freedom ($F_{tab}\ 0.05(9,8) = 3.39$) at 95%
of confidence, and $p$-value was lower than 0.05 (0.0003). Therefore, we can affirm that the quadratic model describes significantly the variation of experimental response. Furthermore, the lack of fit was non-significant, once the tabulated $F$-value ($F_{tab} 0.05 (5,3) = 9.01$) is higher than calculated value (7.11), and the $p$-value is higher than 0.05 (Table S3).

Fig. 1 shows the correlation between the predicted values versus actual (or experimental) values (Fig. 1a), which indicates the quality of the model to predict the response, and the distribution of residues (Fig 1b). According to Fig. 1a, points distributed close to the solid line show a good correlation between the experimental data and predicted values by the quadratic model. The determination coefficient ($R^2$) was 0.9485, which indicates the model describes 94.85% of total variance around the average, leaving only 5.15% of residues. The distribution of residues left by quadratic model is shown in Fig. 1b. According to results, residues showed low values and a random distribution without displaying a systematic distribution, confirming that the model is significant [13,34].

Figure 1

3.4. Response surfaces

The interaction between two variables (maintaining the third in the central level) and their effects on the response were investigated from tridimensional response surfaces, and the profiles are shown in Fig. 2. As can be seen, the highest values of response ($\ln S_{BET}$) and consequently surface area values were observed when the factors are in their superior levels. Fig. 2a-b show the behavior of response in relation of the temperature versus the water:precursor ratio (Fig. 2a) and time (Fig. 2b). The temperature ($x_1$) was the most significant factor (vide $F$-value in Table S2 and Eq. 8), thus the inclination of surface is more pronounced for this factor. On the other hand, the water:precursor ratio factor ($x_3$) was non-significant, which can be observed in Fig. 2b, since variation from the inferior level to the superior level did not significantly influence on the response. Fig. 2c shows the
response values in relation to time ($x_2$) and water:precursor ($x_3$) factors. The concave profile of surface is due the significance of quadratic term $x_2^2$ (Eq. 8), additionally, it can be observed that the maximum value of $\ln S_{BET}$, and consequently the highest value of surface area, was observed around 200 min.

**Figure 2**

3.5. Optimization

The optimization of hydrochar preparation was performed from RSM and desirability function. The desirability function is based on hypothesis that all parameters involved in the quality of a final product must be contained into a set of values limited by the function. This condition is possible converting the responses to a composite function [35]. Desirably function allows to determine the ideal value for all studied variables, including the priorities of researcher (maximize or minimize a response). The range of values possible from the function is 0 to 1. If the value of desirability is 0, the response is completely undesired, however if the value of desirability is 1, the process was totally optimized [36].

The software Design Expert® provided 22 optimization conditions within the experimental range studied. Among the conditions, the optimization was performed from condition which provided the higher desirability value (0.97). This condition corresponds to temperature of 210 °C, time of 243 min and water:precursor ratio of 3.4:1 (v:wt); and the suggested value of $S_{BET}$ found from the model for the response ($\ln S_{BET}$) was 33.30 m$^2$ g$^{-1}$. The hydrochar obtained in the optimized conditions was labeled as HC$_{op}$. Besides condition with best desirability value, other condition was selected with objective to evaluate the model's robustness, and the experimental values of $S_{BET}$ obtained for both selected conditions are compiled in Table S4. According to results, the value of $S_{BET}$ proposed by the model and the value experimentally obtained from the optimal condition, showed good concordance each other, which can be confirmed from the low value of variation coefficient ($\Delta = 6.04\%$). The second condition presented a value of variation coefficient of 12.39%; this difference more
accentuated is related with low value of $S_{BET}$ and detection limit of the surface area analyzer equipment.

3.6. Characterization of optimized hydrochar ($HC_{op}$)

3.6.1. Analyses of inorganic elements

The analyses of inorganic elements were performed aiming to evaluate the contents of some macro- and micronutrients present in the composition of $HC_{op}$. Table 3 shows the results for the raw material and $HC_{op}$. According to results, the raw material has significant contents of macronutrients Mg, Ca, K, N, P and S and micronutrients Fe, Cu, Mn, Zn and B. After HCT, the $HC_{op}$ showed different contents of some elements when compared to the raw material. Contents of some elements, such as Mg, K, Mn and Zn decreased with HCT, while Fe, Cu and Ca increased. This can be due the solubility of some elements, which were dissolved into solution during the degradation processes, while others formed oxides/hydroxides and precipitated together with the $HC_{op}$ mud. Elements as N, P, S and B did not show change in their contents; possibly, they got retained in the material’s portion that was not degraded.

Table 3

3.6.2. $N_2$ adsorption and desorption isotherms

Fig. 3 shows the $N_2$ adsorption and desorption isotherms of $HC_{op}$. According classification criteria of IUPAC (International Union of Pure and Applied Chemistry), the $HC_{op}$ isotherm can be classified as Type III with hysteresis [37]. The isotherm shows a convex profile with low amount of $N_2$ adsorbed up to relative pressure ($p/p^o$) of 0.5, followed by increase of $N_2$ adsorbed amount at high relative pressure values, which is characteristic of capillary condensation step in mesoporous structure. The isotherm profile obtained herein is similar than those reported by Zhu et al. [38], who prepared hydrochars from the Salix psammophila. The $HC_{op}$ showed $V_T$ of 0.140 cm$^3$ g$^{-1}$, absence of
$V_p$ and $D_p$ of 17.8 nm, indicating that material has mesoporosity features. The insert in Fig. 3 shows the pore size distribution for HC$_{op}$. It is possible to observe that material has a wide range of pore distribution, with the maximum distribution around of 178.3 Å.

**Figure 3**

Table 4 shows the experimental parameters used for preparation of hydrochars from different precursors, and the $S_{BET}$ values found. As can be seen, the $S_{BET}$ value of HC$_{op}$ is higher than others hydrochars reported in the literature; although it has been prepared from milder conditions, demonstrating the importance and effectiveness of the optimization process.

**Table 4**

### 3.6.3. FT-IR analysis

The surface groups present on raw material and HC$_{op}$ were investigated from FT-IR analysis and the obtained spectra are shown in Fig. 4. The spectra of raw material and HC$_{op}$ showed similar profiles, indicating the biomass structure (raw material) was not totally decomposed under the experimental conditions selected. However, it is possible to observe a decrease of intensity of the bands centered at ca. 1620 and 1163 cm$^{-1}$.

**Figure 4**

The broadband observed at ca. 3500 cm$^{-1}$ can be assigned to overlapping of O-H (from the phenol groups of hemicellulose, cellulose and lignin) and N-H stretching vibration. The band at ca. 2970 cm$^{-1}$ can be attributed to stretching vibration of C-H bonding, which is characteristic of aliphatic carbon. The bands at region of ca. 1700 and 1600 cm$^{-1}$ can be assigned to stretching vibration of C=C characteristic to aromatics rings of lignin, and C=O corresponding to carbonyl, quinone, ester or
carboxyl groups. The bands distributed between \textit{ca.} 1465 and 1378 cm\(^{-1}\) can be assigned to deformation of C-H and C-O, respectively, present on structure of cellulose and hemicellulose, while the broadband at \textit{ca.} 1160 cm\(^{-1}\) can be attributed to C-O stretching vibration characteristic to glycosidic linkages between sugar units. The presence of these bands in the HC\textsubscript{op} spectrum provides further support to confirm the presence of cellulose and lignin in the hydrochar structure. The broadband at \textit{ca.} 600 cm\(^{-1}\) is characteristic to out-of-plane angular deformities of benzene derivatives [11,31,39].

3.6.4. SEM analysis

The SEM images were obtained for raw material and HC\textsubscript{op} in order to evaluate the changes in the morphological features of materials (Fig. 5). As can be seen in Fig. 5a, the raw material presented a rigid and compact morphology without apparent cavities or any porous structure. On the other hand, the SEM image of HC\textsubscript{op} (Fig. 5b) showed a surface with significant modifications. Therefore, it is possible to observe the hydrothermal carbonization promoted the development of rudimentary porosity through the formation of cavities with different size, which are distributed across the surface of the HC\textsubscript{op}. The rudimentary porosity can be related to increase of surface area of the HC\textsubscript{op} in comparison with the raw material. Additionally, the increase in the surface area value of HC\textsubscript{op} can lead to an increase of binding sites, which are suitable for interaction with adsorbate.

Figure 5

3.6.5. TGA analysis

TG and DTG curves of raw material and HC\textsubscript{op} are shown in Fig. 6. It can be seen from the results that the weight loss of raw material is different of HC\textsubscript{op}. The raw material (Fig. 6a) showed a weight loss of about 50\% between 150 and 320 °C. In this region occurs the decomposition of hemicellulose and cellulose [8,31,40]. At higher temperatures, it can be observed a gradual weight
loss and a remaining mass about of 20 % at 800 °C. This value is in accordance with TGA analysis reported by Nabais et al. [39], who studied coffee husk. The TG curve for HC$_{op}$ (Fig. 6b) showed a remaining mass of 31% at 800 °C and a displacement of weight loss peak for higher temperatures (ca. 360 °C). This displacement can be related to the experimental factors investigated in the optimization processes. Gao et al. [41] reported that high times of HCT favor the hydrolysis of hemicellulose and cellulose, and thus assigning high thermal resistance and surface area for the hydrochars. On the other hand, Pala et al. [40] reported that high temperatures of HCT promote recombination reactions (repolymerization), providing a higher thermal stability of materials. These results are in accordance with chemometrics studies, once the $x_1$ and $x_2$ terms (Eq. 8) demonstrated that keeping the temperature and time in their superior levels, occurs an increase in the $S_{BET}$ value, which can be due to the effective hydrolysis of raw material constituents.

**Figure 6**

### 3.6.6. pH$_{PZC}$

The pH$_{PZC}$ of materials is a very important parameter for understanding the adsorption mechanisms. The pH$_{PZC}$ value is usual to predict the predominant surface charge on adsorbents according to the solution pH. Therefore, for solution pH $<$ pH$_{PZC}$, the adsorbent’s surface is predominantly positively charged, and for solution pH $>$ pH$_{PZC}$, the adsorbent’s surface is predominantly negatively charged [42]. In this sense, the knowledge of surface charge of the adsorbent and ionic features of the adsorbate, allows predicting whether there is electrostatic interaction between them, so solution pH can favor or not the adsorption process. Fig. S1 shows the plot of pH$_{PZC}$ for HC$_{op}$. According to the data, it can be seen pH$_{PZC}$ value of HC$_{op}$ was found to be 5.1, indicating the acid features of the material’s surface. From this value, it is possible to estimate that the material’s surface will has predominance of positive charges for solution pH lower than 5.1, and predominance of negative charges for solution pH higher than 5.1.
3.7. Adsorption studies

3.7.1. Effect of pH

The solution pH is an important factor in the adsorption processes. The effect of pH in the adsorption of MB onto HC$_{op}$ is shown in Fig. S2. As can be seen, the highest adsorption capacities ($q_e$) were observed at pH values higher than 4.0. These results agree with $pH_{PZC}$ (5.1), which predicts that for $pH_{solution} > pH_{PZC}$ the material's surface presents negative character. Therefore, highest values of pH favor the MB adsorption on the HC$_{op}$ from the electrostatic interactions between adsorbent and adsorbate. Considering the small difference for pH values higher than 5.0, the natural pH of the dye solution (5.50) was chosen for subsequent adsorption studies.

3.7.2. Adsorption kinetic

The kinetic data of MB adsorption onto HC$_{op}$ from the different initial concentrations and the nonlinear fits of pseudo-first order, pseudo-second order, and Elovich models are shown in Fig. S3. According to results, it can be observed the adsorption rate for three different MB l concentrations (100, 300 and 500 mg L$^{-1}$) were higher in the first 60 min of process, and the systems reached the equilibrium after 120 min. The kinetic parameters, determination coefficients ($R^2$) and $\Delta q_e$ of models fitted to the experimental data are listed in Table 5. Evaluating the parameters for three proposed kinetic models, the Elovich model gave the best fit to the experimental kinetic data for all studied concentrations, once it showed the highest $R^2$ values and the lowest $\Delta q_e$ values. The Elovich model assumes that the solid surface is energetically heterogeneous and neither desorption nor the interaction between the adsorbed species could affect the kinetics of adsorption at low surface coverage. Additionally, the $\alpha$ parameter is related to the initial adsorption rate and $\beta$ to the desorption rate [43,44]. From the values displayed in Table 5, it can be observed for three MB concentrations that $\alpha$ values (ranged from 5.48 to 6.99 mg g$^{-1}$ min$^{-1}$) were found to be higher than $\beta$ values (ranged from 0.131 to 0.304 g mg$^{-1}$ min$^{-1}$), indicating the effective interaction between adsorbent and
adsorbate, and evidencing the viability of the adsorption of MB onto HC\textsubscript{op}.

The Weber-Morris intra-particle diffusion model was fitted to the kinetic experimental data, and the linear profiles obtained by the plots of \(q_t\) vs. \(t^{1/2}\) for three initial MB concentrations are shown in Fig. S3d. From the results, it can be seen multi-linear plots, suggesting that the adsorption of MB onto HC\textsubscript{op} occurs from a three-step process and the intra-particle diffusion is not the rate-limiting step, once the linear plot did not pass through the origin. The first step consists in the external mass transfer (film diffusion) of MB to HC\textsubscript{op} surface. The second step represents the intra-particle diffusion, and the third step the final equilibrium stages [44,45]. The \(k_{id}\) and \(C_i\) values were obtained from the slopes and intercepts of the plots, respectively, and the values were compiled in Table 5. As shown in Table 5, the \(k_{id2}\) values increased (0.17-24.64 mg g\(^{-1}\) min\(^{-1/2}\)) with the increase of the initial MB concentration, indicating a faster intra-particle diffusion for high initial concentrations. Additionally, \(k_{id}\) and \(C_i\) also increased with the increase of initial concentration, which can be due to the increase in the boundary layer thickness and driving forces of adsorption associated with the increasing dye concentration in solution [44].

**Table 5**

3.7.3. Adsorption isotherm and thermodynamic study

The isotherm models have been used to describe, in quantitative terms, the adsorption of solutes on solids at constant temperatures. Studies involving adsorption isotherms can indicate the amount of a certain solute adsorbed on the adsorbent surface, as a function of the equilibrium concentration of solute in solution. From the adsorption isotherm, it is possible to understand as the adsorbent will adsorb the solute, and if the solution purification can be reached, as well as the estimation of maximum adsorption capacity and economic viability. Fig. S4a shows experimental data and nonlinear fits of Langmuir, Freundlich and Dubinin-Radushkevich models. According to results, an increase of MB initial concentration promotes an increase of \(q_e\) values. Fig. S4b illustrates
the separation factor ($R_L$) for Langmuir isotherm, which can be used to determine if the adsorption is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) [6]. The results indicate that adsorption is favorable for all initial concentration range investigated; presenting $R_L$ values lower than 1.0.

The isothermal parameters, $R^2$ and $\Delta q_e$ are shown in Table 6. Evaluating $R^2$ and $\Delta q_e$ parameters, the three isotherm models showed values of $R^2 > 0.91$, and $\Delta q_e$ values ranged from 9.22 to 27.2%. The results indicate the Langmuir model is the best to describe the equilibrium experimental data.

**Table 6**

The Freundlich model considers that adsorption occurs in multilayers and the active sites on the adsorbent are distributed unevenly and have different energies. In addition, $n_F$ parameter is used to evaluate if the adsorption process is favorable and if it occurs from a linear ($n_F = 1$), chemical ($n_F < 1$) or physical process ($n_F > 1$) [27]. The $n_F$ value was found to be 4.74, indicating that the physical adsorption is favorable.

The Dubinin-Radushkevich model (D-R) provides information about the kind of adsorption and the nature of interaction between adsorbate and adsorbent. The sorption average energy ($E$, kJ mol$^{-1}$) corresponds to the free energy involved in the transference of 1 mol of solute from the bulk of the solution until the adsorbent’s surface. If the adsorption process occurs via weak bonds (van der Waals interaction or physisorption), $E$ values range from 4-8 kJ mol$^{-1}$; hydrogen bonds, $E$ ranging is from 2-40 kJ mol$^{-1}$; or chemisorption, with $E$ ranging from 60-80 kJ mol$^{-1}$ [46]. According to results (Table 6), $E$ value was 19.61 kJ mol$^{-1}$, indicating the predominance of hydrogen bonds in the adsorption mechanism.

The Langmuir model assumes that adsorption occurs in monolayer, and just one adsorbate molecule can be adsorbed by an available binding site on the adsorbent surface. Herein, the monolayer
adsorption capacity of MB adsorption ($Q_m$) was found to be 35.00 mg g$^{-1}$. This value is comparable to others similar adsorbents materials reported in the literature, which were not submitted to activation processes, such as: biochars prepared from the rice husk ($Q_m = 40.58$ mg g$^{-1}$) [47], anaerobic digestion residues (9.50 mg g$^{-1}$), palm husk (2.66 mg g$^{-1}$), eucalyptus (2.06 mg g$^{-1}$) [48] and spent coffee grounds (18.7 mg g$^{-1}$) [49].

The thermodynamic parameters were calculated from equations listed in Table S1 and the results are compiled in Table S5. The Gibbs free energy change ($\Delta G^\circ$) increased (-11.56 to -17.80 kJ mol$^{-1}$) with increase in the temperature, indicating that adsorption of MB onto HC$_{op}$ becomes more favorable at higher temperature. Additionally, negative values of $\Delta G^\circ$ confirm the feasibility and the spontaneous nature of the adsorption process. The values of enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) were estimated from the plot of $\ln K_c$ vs. $1/T$, and they were found to be 49.79 kJ mol$^{-1}$ and 204.27 J K$^{-1}$ mol$^{-1}$ (Table S5), respectively. The positive signal of $\Delta H^\circ$ indicates the endothermic nature of the adsorption of MB on HC$_{op}$, whereas its value suggests that the process is driven by physisorption, once it was less than 84 kJ mol$^{-1}$ [50]. The positive value of $\Delta S^\circ$ indicates the higher randomness for the MB-HC$_{op}$ system.

4. Conclusions

Hydrochar was successfully obtained from coffee husk, and the preparation conditions optimized from RSM. The significant HCT factors on surface area development of hydrochar were the time and temperature. The hydrochar obtained in the optimized conditions (HC$_{op}$) presented high surface area, even being prepared from milder conditions, when compared to others hydrochars reported in literature, indicating the effectiveness of optimization process. Significant differences were observed between physicochemical properties of raw material and HC$_{op}$. The adsorption studies demonstrated that HC$_{op}$ has good monolayer adsorption capacity for MB and the process is endothermic and spontaneous. Additionally, it was observed that the interaction between adsorbent and adsorbate occurs preferably by physisorption, however, H-bonding also plays an important role
in the process. Therefore, coffee husks present high potential as precursor of hydrochars with well-developed surface area.

Acknowledgements

The authors acknowledge the financial support provided by CAPES, CNPq and Fundação Araucária—Brazil.

References


[48] L. Sun, S. Wan, W. Luo, Biochars prepared from anaerobic digestion residue, palm bark, and


Figure legends

**Fig.1** Correlation between the predicted values versus actual values (a) and plot of the residues versus experimental order.

**Fig. 2** Three-dimensional response surface for the \( \ln S_{BET} \): activation time versus temperature (a), water: precursor ratio versus temperature (b) and water: precursor ratio versus time (c).

**Fig. 3** \( \text{N}_2 \) adsorption (closed symbols) and desorption (opened symbols) isotherm at 77 K. The insert shows the pore size distribution for \( \text{HC}_{\text{op}} \) material.

**Fig. 4** FT-IR spectra of raw material and \( \text{HC}_{\text{op}} \).

**Fig. 5** SEM images of coffee husk (a) and \( \text{HC}_{\text{op}} \) (b).

**Fig. 6** TGA and DTG analysis of raw material (a) and \( \text{HC}_{\text{op}}\)(b).
Figure 1

(a) $R^2 = 0.9485$

Predicted values (\(\ln S_{BET}\)) vs. Actual values (\(\ln S_{BET}\))

(b) Internally studentized residuals

Run number

-3.0
-1.5
0.0
1.5
3.0

0 2 4 6 8 10 12 14 16 18
Figure 2
Figure 3

![Graph showing adsorbed volume vs. relative pressure](image)

- **Adsorbed volume (cm³ g⁻¹)**
- **Relative pressure (p/p₀)**

Inset: Pore diameter (Å) vs. dV/dP.
Figure 4

![Graph showing the transmittance of raw material and HC against wavenumber.](image)

- Raw material
- HC<sub>np</sub>

Transmittance (a.u.) vs. Wavenumber (cm<sup>-1</sup>)

Wavenumber (cm<sup>-1</sup>)

4000 3500 3000 2500 2000 1500 1000 500

Transmittance (a.u.)

4000 3500 3000 2500 2000 1500 1000 500
Figure 5
Figure 6

[Diagram showing weight loss and temperature against DTG (% min⁻¹) for two different conditions (a) and (b)].

Weight loss (%) vs Temperature (°C)

DTG (% min⁻¹) vs Temperature (°C)
Table 1. Independents factors and their codified and real levels.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Codified levels</th>
<th></th>
<th>Real levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-1.68 (-α)</td>
<td>-1</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>165</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>188</td>
<td>188</td>
</tr>
<tr>
<td></td>
<td>+1.68 (+α)</td>
<td>210</td>
<td>210</td>
</tr>
<tr>
<td>Temperature (°C): $(x_1)$</td>
<td></td>
<td></td>
<td>225</td>
</tr>
<tr>
<td>Time (min): $(x_2)$</td>
<td>20</td>
<td>77</td>
<td>20</td>
</tr>
<tr>
<td>Water:precursor ratio (v:wt): $(x_3)$</td>
<td>1.0</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Table 2 Experimental design with actual and codified levels, results for yield and surface area (S\textsubscript{BET}) as well as the analyzed responses $y_1 (\ln S_{BET})$.

<table>
<thead>
<tr>
<th>Run</th>
<th>$X_1^a(x_1)^b$</th>
<th>$X_2^a(x_2)^b$</th>
<th>$X_3^a(x_3)^b$</th>
<th>Yield (%)</th>
<th>$S_{BET}$ (m\textsuperscript{2} g\textsuperscript{-1})\textsuperscript{c}</th>
<th>$y_1^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>165(-1)</td>
<td>77(-1)</td>
<td>1.6(-1)</td>
<td>58.18</td>
<td>2.90</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>210(+1)</td>
<td>77(-1)</td>
<td>1.6 (-1)</td>
<td>57.00</td>
<td>25.10</td>
<td>3.22</td>
</tr>
<tr>
<td>3</td>
<td>165(-1)</td>
<td>243(+1)</td>
<td>1.6(-1)</td>
<td>55.67</td>
<td>5.76</td>
<td>1.75</td>
</tr>
<tr>
<td>4</td>
<td>210(+1)</td>
<td>243(+1)</td>
<td>1.6 (-1)</td>
<td>53.85</td>
<td>29.50</td>
<td>3.39</td>
</tr>
<tr>
<td>5</td>
<td>165(-1)</td>
<td>77(-1)</td>
<td>3.4(+1)</td>
<td>56.91</td>
<td>4.34</td>
<td>1.47</td>
</tr>
<tr>
<td>6</td>
<td>210(+1)</td>
<td>77(-1)</td>
<td>3.4 (+1)</td>
<td>54.19</td>
<td>15.00</td>
<td>2.71</td>
</tr>
<tr>
<td>7</td>
<td>165(-1)</td>
<td>243(+1)</td>
<td>3.4 (+1)</td>
<td>52.52</td>
<td>12.40</td>
<td>2.52</td>
</tr>
<tr>
<td>8</td>
<td>210(+1)</td>
<td>243(+1)</td>
<td>3.4 (+1)</td>
<td>52.96</td>
<td>31.22</td>
<td>3.60</td>
</tr>
<tr>
<td>9</td>
<td>150 (-1.68)</td>
<td>160(0)</td>
<td>2.5(0)</td>
<td>57.84</td>
<td>2.96</td>
<td>1.09</td>
</tr>
<tr>
<td>10</td>
<td>225 (+1.68)</td>
<td>160(0)</td>
<td>2.5 (0)</td>
<td>52.79</td>
<td>28.30</td>
<td>3.34</td>
</tr>
<tr>
<td>11</td>
<td>188(0)</td>
<td>20 (-1.68)</td>
<td>2.5 (0)</td>
<td>63.70</td>
<td>2.05</td>
<td>0.72</td>
</tr>
<tr>
<td>12</td>
<td>188 (0)</td>
<td>300 (+1.68)</td>
<td>2.5 (0)</td>
<td>56.39</td>
<td>17.40</td>
<td>2.86</td>
</tr>
<tr>
<td>13</td>
<td>188 (0)</td>
<td>160(0)</td>
<td>1 (-1.68)</td>
<td>58.47</td>
<td>12.60</td>
<td>2.54</td>
</tr>
<tr>
<td>14</td>
<td>188 (0)</td>
<td>160 (0)</td>
<td>4 (+1.68)</td>
<td>52.74</td>
<td>15.50</td>
<td>2.74</td>
</tr>
<tr>
<td>15</td>
<td>188 (0)</td>
<td>160 (0)</td>
<td>2.5 (0)</td>
<td>55.39</td>
<td>16.90</td>
<td>2.83</td>
</tr>
<tr>
<td>16</td>
<td>188 (0)</td>
<td>160 (0)</td>
<td>2.5 (0)</td>
<td>54.99</td>
<td>13.77</td>
<td>2.16</td>
</tr>
<tr>
<td>17</td>
<td>188 (0)</td>
<td>160 (0)</td>
<td>2.5 (0)</td>
<td>55.89</td>
<td>13.00</td>
<td>2.57</td>
</tr>
<tr>
<td>18</td>
<td>188 (0)</td>
<td>160 (0)</td>
<td>2.5 (0)</td>
<td>52.52</td>
<td>16.30</td>
<td>2.79</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Actual values for: $X_1$ = carbonization temperature (°C); $X_2$ = time (min) and $X_3$ = water:precursor ratio (v:wt); \textsuperscript{b}coded values; \textsuperscript{c}surface area (m\textsuperscript{2} g\textsuperscript{-1}) and \textsuperscript{d}natural logarithm of surface area.
Table 3. Macro- and micronutrients analysis for raw material and HC_{op}.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Raw material</th>
<th>HC_{op}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (g kg(^{-1}))</td>
<td>1.92</td>
<td>0.350</td>
</tr>
<tr>
<td>Ca (g kg(^{-1}))</td>
<td>4.00</td>
<td>5.12</td>
</tr>
<tr>
<td>K (g kg(^{-1}))</td>
<td>7.06</td>
<td>0.560</td>
</tr>
<tr>
<td>N (g kg(^{-1}))</td>
<td>19.6</td>
<td>21.77</td>
</tr>
<tr>
<td>P (g kg(^{-1}))</td>
<td>0.47</td>
<td>0.510</td>
</tr>
<tr>
<td>S (g kg(^{-1}))</td>
<td>1.10</td>
<td>0.890</td>
</tr>
<tr>
<td>Fe (mg kg(^{-1}))</td>
<td>34.8</td>
<td>134.0</td>
</tr>
<tr>
<td>Cu (mg kg(^{-1}))</td>
<td>4.40</td>
<td>7.67</td>
</tr>
<tr>
<td>Mn (mg kg(^{-1}))</td>
<td>65.8</td>
<td>35.5</td>
</tr>
<tr>
<td>Zn (mg kg(^{-1}))</td>
<td>5.77</td>
<td>2.80</td>
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<tr>
<td>B (mg kg(^{-1}))</td>
<td>91.4</td>
<td>85.1</td>
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Table 4. Experimental parameters used for different researcher for preparation of hydrochars from different precursors, and respective $S_{BET}$ values.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Ratio (v:wt)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salix psammophila</td>
<td>7.16</td>
<td>300</td>
<td>-</td>
<td>0.0125</td>
<td>[36]</td>
</tr>
<tr>
<td>Food residues</td>
<td>6.07-1.01</td>
<td>250-350</td>
<td>20</td>
<td>4.00</td>
<td>[5]</td>
</tr>
<tr>
<td>Tannins</td>
<td>&gt; 10.00</td>
<td>130-200</td>
<td>60-8640</td>
<td>32.00</td>
<td>[37]</td>
</tr>
<tr>
<td>Sunflower stem</td>
<td>31.30</td>
<td>200</td>
<td>1200</td>
<td>20.00</td>
<td>[38]</td>
</tr>
<tr>
<td>Commercial cellulose</td>
<td>27.80</td>
<td>230</td>
<td>360</td>
<td>0.01</td>
<td>[31]</td>
</tr>
<tr>
<td>Palm bunches</td>
<td>8.03</td>
<td>250</td>
<td>20</td>
<td>10.00</td>
<td>[39]</td>
</tr>
<tr>
<td>Palm shell</td>
<td>0.126</td>
<td>180</td>
<td>30</td>
<td>1.60 (wt.%)</td>
<td>[29]</td>
</tr>
<tr>
<td>Coffee husk</td>
<td><strong>31.30</strong></td>
<td><strong>210</strong></td>
<td><strong>243</strong></td>
<td><strong>3.41</strong></td>
<td>Present work</td>
</tr>
</tbody>
</table>
Table 5. Kinetic parameters of pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion models for MB adsorption onto HCop.

<table>
<thead>
<tr>
<th>Initial concentration (mg L(^{-1}))</th>
<th>100</th>
<th>300</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_{e,exp} ) (mg g(^{-1}))</td>
<td>20.95</td>
<td>35.82</td>
<td>39.28</td>
</tr>
<tr>
<td><strong>Pseudo-first order</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_e ) (mg g(^{-1}))</td>
<td>17.97</td>
<td>33.07</td>
<td>35.09</td>
</tr>
<tr>
<td>( k_1 ) (min(^{-1}))</td>
<td>7.76 \times 10^{-2}</td>
<td>5.89 \times 10^{-2}</td>
<td>4.52 \times 10^{-2}</td>
</tr>
<tr>
<td>( h_0 ) (mg g(^{-1}) min(^{-1}))</td>
<td>25.06</td>
<td>64.42</td>
<td>55.59</td>
</tr>
<tr>
<td>( \Delta q_e ) (%)</td>
<td>17.93</td>
<td>18.86</td>
<td>26.32</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.8769</td>
<td>0.9471</td>
<td>0.8805</td>
</tr>
<tr>
<td><strong>Pseudo-second order</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_e ) (mg g(^{-1}))</td>
<td>19.65</td>
<td>36.62</td>
<td>39.46</td>
</tr>
<tr>
<td>( k_2 ) (g mg(^{-1}) min(^{-1}))</td>
<td>5.47 \times 10^{-3}</td>
<td>2.15 \times 10^{-3}</td>
<td>1.52 \times 10^{-3}</td>
</tr>
<tr>
<td>( h_0 ) (mg g(^{-1}) min(^{-1}))</td>
<td>2.11</td>
<td>2.88</td>
<td>2.36</td>
</tr>
<tr>
<td>( \Delta q_e ) (%)</td>
<td>13.16</td>
<td>12.68</td>
<td>18.54</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9419</td>
<td>0.9798</td>
<td>0.9379</td>
</tr>
<tr>
<td><strong>Elovich</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha ) (mg g(^{-1}) min(^{-1}))</td>
<td>6.99</td>
<td>7.39</td>
<td>5.48</td>
</tr>
<tr>
<td>( \beta ) (g mg(^{-1}) min(^{-1}))</td>
<td>0.304</td>
<td>0.149</td>
<td>0.131</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9909</td>
<td>0.9899</td>
<td>0.9783</td>
</tr>
<tr>
<td>( \Delta q_e ) (%)</td>
<td>7.14</td>
<td>12.26</td>
<td>12.22</td>
</tr>
<tr>
<td><strong>Intra-particle diffusion</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>First stage</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_{id} ) (mg g(^{-1}) min(^{-1/2}))</td>
<td>4.03</td>
<td>5.94</td>
<td>5.39</td>
</tr>
<tr>
<td>( C_1 ) (mg g(^{-1}))</td>
<td>0.07</td>
<td>0.17</td>
<td>0.36</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9989</td>
<td>0.9971</td>
<td>0.9900</td>
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<tr>
<td><strong>Second stage</strong></td>
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</tr>
<tr>
<td>( k_{id} ) (mg g(^{-1}) min(^{-1/2}))</td>
<td>1.32</td>
<td>3.20</td>
<td>2.19</td>
</tr>
<tr>
<td>( C_2 ) (mg g(^{-1}))</td>
<td>5.74</td>
<td>5.83</td>
<td>9.41</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9806</td>
<td>0.9958</td>
<td>0.9989</td>
</tr>
<tr>
<td><strong>Third stage</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_{id} ) (mg g(^{-1}) min(^{-1/2}))</td>
<td>0.70</td>
<td>0.74</td>
<td>1.26</td>
</tr>
<tr>
<td>( C_2 ) (mg g(^{-1}))</td>
<td>10.36</td>
<td>24.64</td>
<td>20.79</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9759</td>
<td>0.9519</td>
<td>0.8084</td>
</tr>
</tbody>
</table>
Table 6. Isothermal parameters of Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models for MB adsorption onto HC_op.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>D-R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_m = 34.85 \text{ mg g}^{-1}$</td>
<td>$K_F = 9.190 \text{ L mg}^{-1}$</td>
<td>$Q_m = 33.02 \text{ mg g}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$K_L = 0.084 \text{ L mg}^{-1}$</td>
<td>$n_F = 4.74$</td>
<td>$K_{DR} = 1.3 \times 10^{-3} \text{ mol}^2 \text{ J}^{-2}$</td>
<td></td>
</tr>
<tr>
<td>$R_L = 0.3226-0.0232$</td>
<td>$R^2 = 0.9668$</td>
<td>$E = 19.61 \text{ kJ mol}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>$R^2 = 0.9537$</td>
<td>$R^2 = 0.9111$</td>
<td></td>
</tr>
<tr>
<td>$\Delta q = 9.22%$</td>
<td>$\Delta q = 27.2%$</td>
<td>$\Delta q = 16.2%$</td>
<td></td>
</tr>
</tbody>
</table>