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Valorization of lignocellulosic agave residues via pyrolysis and its use as adsorbent for methylene blue removal

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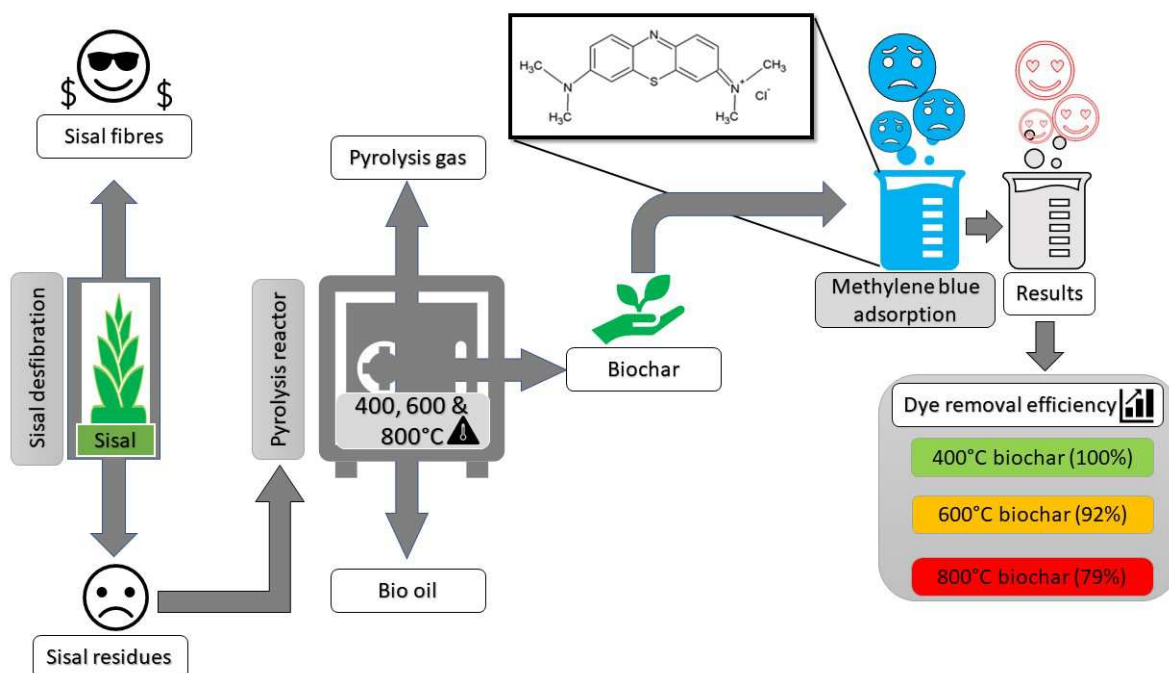
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Abstract

The economic exploitation of sisal (*Agave sisalana*) fibers leads to the generation of underutilized waste. Therefore, technologies must be developed to mitigate the environmental impacts caused by inadequate waste disposal and ensure more income from sisal exploration. The present study investigated the potential of agave residues in producing biochar with high adsorbent capacity via slow pyrolysis. Hybrid Itaporanga, Hybrid Bahia, and Mutant-1 hybrid agave varieties were used as precursors and methylene blue (MB) dye was used as a solute. In general, agave residues presented similar contents of lignin (12.1-13.2%) and ash (10.3-13.9%), while the greatest differences were recorded in the values of holocellulose (31.4%-42.4%) and extractives (23.2%-33.4%). The increase in temperature favored an increase in the surface area and volume of micropores in the biochar; however, the adsorption capacity of MB dye was reduced. The pseudo-second-order models effectively adjusted the adsorption kinetics. The Hybrid Itaporanga biochar obtained at 400 °C outperformed the other biochar, presenting static (80 mg.g⁻¹) and dynamic (180 mg.g⁻¹) adsorption values. Thus, thermochemical valorization of agave residue is attractive to obtain a cheap and environmentally friendly adsorbent.

Keywords: waste biomass; biochar; thermochemical valorization

Graphical abstract



1. Introduction

The use of Crassulacean Acid Metabolism (CAM) plants as an abundant source of lignocellulosic biomass has drawn the attention of researchers recently due to their high energy potential [1], low-cost biomass production, adaptation to drylands, and survival with little or no rainfall for long periods. CAM plants can sequester carbon dioxide and photosynthesize more efficiently under water-limited environments than plants with C3 and C4 metabolism [2]. Among the different types of CAM plants, agave species stand out for their economic appeal: *Agave tequilana* and *Agave sisalana*. *Agave tequilana* is used to prepare tequila, a distilled alcoholic drink that is a symbol of Mexico. *Agave sisalana* is widely used to generate natural fibers for handicrafts and has Brazil as one of its main global producers[3].

A. sisalana was brought to Brazil from the United States and has been planted extensively, especially in the semiarid region. Between 1980 and 1990, Brazil exported more than 200 thousand tons of sisal fiber yearly [4]. In 2021, Brazil produced around 85 thousand tons of agave fiber and exported 65 thousand tons, generating around 100 million dollars in the poorest region of Brazil. This lower production occurred because of the Covid-19 pandemic, but even so, Brazil continued to be the largest sisal fiber exporter in the world [5]. Around 1 million families and local farmers benefit directly and indirectly from the cultivation, processing and exportation of agave fiber in Brazil's poorest regions [6].

In sisal processing, the primary product is the fiber; however, this process generates a considerable quantity of residues, comprising about 80%-90% of the plant biomass. In Brazil, these residues represent more than 1.8 million tons 80%, liquid and 20% solid bagasse rich in lignocellulose [7], [8]. A part of agave bagasse is used as a low-nutritional quality animal feed source, exclusively offered to livestock animals during drought periods. Thus, most of the residues have no current significant use, being discarded without any application, and their inappropriate disposal generates several environmental problems [9].

Agave residue contains a significant amount of lignocellulose, which can be thermally treated in the absence of oxygen in a process called pyrolysis. Pyrolysis can produce multiple products, such as bio-oil, biochar, and syngas [10], [11][12]. The composition of the phases can be controlled by adjusting some operational parameters, such as final reactor temperature, residence time, heating rate, carrier gas flow, type of reactor, and the nature of biomass used [13], [14] and [3].

Biochar is a source of low-cost carbonaceous material, highly stable and exceptionally resistant to chemical and biological degradation, exhibiting good water and mineral retention capacity [3]. Biochar serves several applications, including biofuel, catalyst support, bioremediation, and to help ameliorate depleted soil nutrition [15]. The generation of biochar is also being touted as a route to decarbonizing the atmosphere [16]. However, without a doubt, water treatment is one of the main destinations for biochar[17].

The effluents from textile industries are characterized by high turbidity and a high load of organic chemical compounds. Dyes are the primary contaminants of these effluents, which are difficult to degrade and highly toxic to the environment, making this effluent one of the most difficult to treat [18]. Therefore,

developing technologies for treating these wastewaters has received increasing attention. Due to its excellent chemical properties and porous structure, biochar has been widely used to remove environmental contaminants, and it can be effective in discoloring contaminated water with a few ppm of dyes [19]. Malike Dizbay-Onat et al., investigated the use of sisal fiber residue (*Agave sisalana*) in the preparation of activated carbon with high surface area and excellent properties in the removal of dyes found in trace amounts in wastewater [20]. Another study using activated charcoal obtained from sisal fiber was carried out by Kahina Bouhadjra when studying textile industrial wastewater, obtaining excellent results removing Cibacron blue dye [21].

Despite the growing literature, some aspects and challenges of agave biochar still need to be addressed. The influence of different sisal hybrids on the adsorptive performance of the biochar has not been previously documented. Also, little is known about how the pyrolysis temperatures affect the sisal residue biochar physicochemical properties and adsorptive capacity. Therefore, the present work was conducted to characterize the chemical composition and physicochemical properties of the residues of three agave hybrid species (Hybrid Itaporanga, Hybrid Bahia, and Mutant-1), evaluating their potential use to produce biochar without any activation and analyzing their performance for the adsorptive removal of methylene blue (MB) dye in synthetic aqueous solutions.

2. Materials and methods

2.1. Chemicals

Hydrated methylene blue ($C_{16}H_{18}ClN_3S \cdot xH_2O$) for analysis was obtained from Neon commercial reagents, and sodium hydroxide (NaOH) acquired from Synth was used to maintain the pH at 9 (buffer), for methylene blue adsorption experiments. All MB dye solutions were obtained using distilled water.

2.2 Preparation and characterization of agave residues

Agave samples were kindly provided by the Embrapa Algodão unit, which is in the city of Monteiro (State of Paraíba, Brazil) (7° 53' 20" S 37° 07' 12" W). The agave samples comprised shredded residues from the Itaporanga, Mutant Bahia, and Mutant-1 varieties. The samples were dried in an air circulation oven at 60 °C for 96 h and then crushed and sieved at 80 mesh.

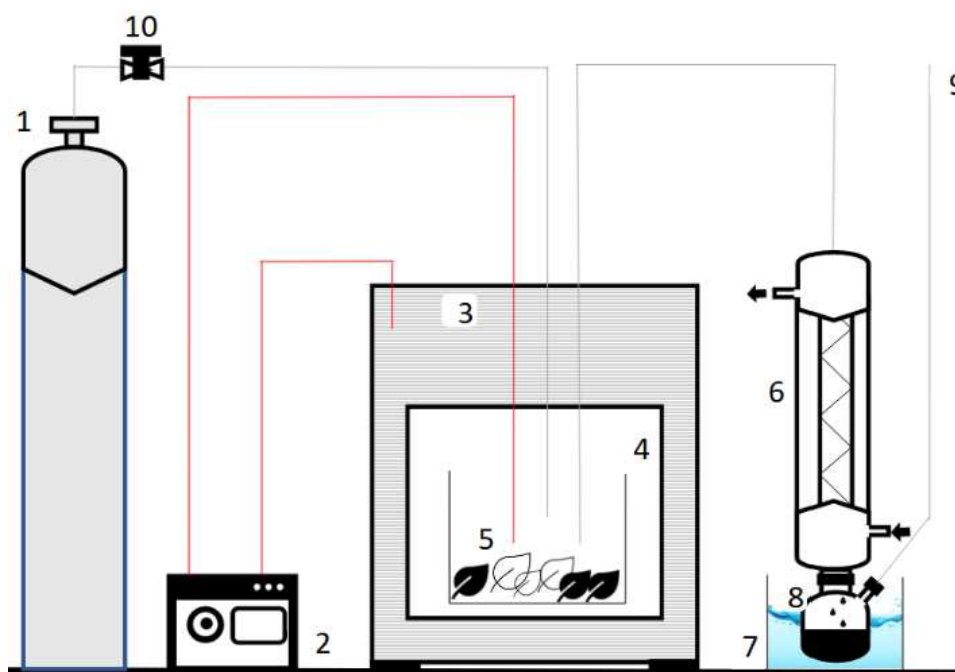
Different physicochemical characterizations were carried out with the agave samples. Elemental analysis was performed on a 2400 SERIES II elemental analyzer (Perkin Elmer), based on the procedures of Dayton and Foust [22]. The percentage of oxygen (O%) is calculated from the difference between the total (100%) and the sum of the carbon, nitrogen, hydrogen, and sulfur contents. The calorific values (LHV and HHV) were measured (in triplicate) in an adiabatic oxygen bomb calorimeter C 2000 (IKA WEBER), according to the ASTM D5865 method [29]. The chemical composition of the agave varieties (moisture, extractives, ash, cellulose, hemicellulose, Klason lignin) was determined using the procedures of Sluiter et al. (2005, 2008a, 2008b). FTIR analyzes were performed on a Bruker Tensor II spectrometer with a range of 4000-850 cm^{-1} and a resolution of 4 cm^{-1} . Thermogravimetric analyzes were also used to characterize

the agave samples. The thermogravimetric analysis was conducted on a TGA SDT Q600 equipment (QA Instruments) under an inert atmosphere (N_2 flow gas rate) and heating rate of $20\text{ }^{\circ}\text{C}.\text{min}^{-1}$.

2.3. Biochar production via pyrolysis

Pyrolysis was carried out in a homemade fixed-bed reactor under an inert environment ($1\text{ L}.\text{min}^{-1}$ of N_2 gas flow rate) with a heating rate of $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$ until the desired temperature (400 , 600 or $800\text{ }^{\circ}\text{C}$). Figure 1 illustrates the apparatus used for the pyrolysis of agave waste. The gases generated in the process passed through an ice bath condenser to obtain bio-oil. After 1 h of process, the biochar samples were collected after cooling in an inert environment and then stored in a desiccator for later use. Bio-oil and bio-oil yields were calculated based on the mass of agave residue used (on a dry basis).

Figure 1. Biochar and bio-oil production from the slow pyrolysis of agave residue. 1-nitrogen gas, 2-temperature control and thermostat, 3- electric furnace 4- stainless steel pyrolysis reactor, 5-biomass, 6-water condenser, 7-water container, 8-water, 9-non condensable gas outlet, 10-gas flow valve.



2.4. Characterization of the biochar from agave residues

The biochar samples were characterized by FTIR. Like agave residues, biochar samples were analyzed on a Bruker Tensor II spectrometer with a range of $4000\text{--}850\text{ cm}^{-1}$ and a resolution of 4 cm^{-1} . Surface area (BET method) and porosity (mesopore and micropore volume) analyzes were carried out on an ASAP 2420 equipment (Micromeritics Instrument Corporation). X-ray fluorescence analyzes on the biochar samples were also carried out. Measurements were performed in vacuum with biochar pressed into an S2 Puma EDXRF spectrometer (Bruker) with 50 W X-ray and HighSense Silicon Drift detector.

2.5. Methylene Blue adsorption experiments

Surface area and porosity analyses were performed on a Surface Area and Porosity Analyzer, model ASAP 2420, manufactured by Micromeritics Instrument Corporation. The surface area of the samples was determined from the N₂ adsorption–desorption isotherms and by using the Brunauer–Emmett–Teller (BET) method. The Barrett–Joyner–Halenda mesopore characteristics and the micropore volume using *t*-plots were also determined. BET analysis was performed for biochar produced at 400 and 600 °C from Hybrid Itaporanga residue.

2.5.1 Batch adsorption experiments

Adsorption experiments were conducted in Erlenmeyer flasks to screen biochar samples with the highest MB dye removal capacity. Biochar samples (50 mg) were added to 25-mL Erlenmeyer flasks containing 10 mL of 100 mg.L⁻¹ MB dye (in Tris-HCl buffer, pH 9.0). The flasks were placed in a shaker at 30 °C and 150 rpm for 24 h, and the supernatants were collected for MB dye quantification. MB dye was quantified in a Genesys UV10 spectrophotometer (ThermoSpectronic, United States) at 665 nm. The adsorption capacity was calculated by Eq 2.

$$E\% = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1)$$

$$q = \frac{V(C_0 - C_e)}{m} \quad (2)$$

Where *E*% is the adsorption efficiency, *q* (mg. g⁻¹) is the amount of adsorbed solute per gram of adsorbent, *C*₀ is the initial concentration of the MB dye, and *C_e* and *C_f* are the equilibrium and final concentrations in mg. L⁻¹. *V* (L) is the volume of the solution, and *m* (g) is the mass of biochar used.

The operational conditions (pH, temperature, time, etc.) were maintained, and only the initial MB dye concentration was changed (25-3000 mg.L⁻¹) in adsorption isotherm experiments. The linearized Freundlich (Eq. 3) and Langmuir (Eq. 4) models were chosen to predict the equilibrium adsorption behavior.

$$\ln q_e = \frac{1}{n} \ln C_e + \ln k_F \quad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (4)$$

The terms *q_e* and *q_{max}* represent the equilibrium adsorption capacity and maximum equilibrium adsorption capacity, respectively (both have the unit mg g⁻¹). The term *K_L* is the Langmuir constant (L g⁻¹), *C_e* is the equilibrium adsorbate concentration (mg L⁻¹), and *K_F* is the Freundlich constant (L g⁻¹). The term *n* is an empirical parameter of the Freundlich model.

Mathematical models also fitted adsorption kinetic data. Pseudo-first-order (Eq. 5) and pseudo-second-order (Eq. 6) mathematical models were linearized and applied according to the methodology of Kaline et al. [23].

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (5)$$

$$\frac{1}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

The terms k_1 and k_2 represent the adsorption constants of the pseudo-first and pseudo-second-order models, respectively.

2.5.2 Column adsorption experiments

Column adsorption experiments were carried out in continuous flow using a TE-BP-01 peristaltic pump (Tecnal, Brazil) and a homemade column. The column had dimensions of 1.0×60.0 cm and a perforated stainless-steel plate to ensure fluid distribution and biochar retention. The experiments were conducted with a volumetric flow rate of $1.8 \text{ mL} \cdot \text{min}^{-1}$, fixed bed height of 6 cm and, MB dye concentration of $500 \text{ mg} \cdot \text{L}^{-1}$. Aliquots were collected for every 10 mL of passing solution and analyzed in a spectrophotometer at 665 nm. The dynamic adsorption capacity (DAC; $\text{mg} \cdot \text{g}^{-1}$) of MB dye was calculated from Eq. 7.

$$DAC = \frac{C_0 V_f - \int_0^{V_f} C \, dV}{m_{ads}} \quad (7)$$

Where C_0 is the initial concentration of the methylene blue solution (mg L^{-1}), V_f is the final volume of the injected solution (mL), and m_{ads} is the adsorbent (biochar) mass (g) as adapted from [24].

3. Results and Discussion

Table 1 presents the elemental analysis, heat of combustion, and characterization of the different agave samples. The carbon content of the Hybrid Bahia residue (35.2%) was slightly higher than the carbon content of the Hybrid Itaporanga (34.2%) and Mutant-1 (34.6%) residues. The highest oxygen content (47.1%) was observed in the Mutant-1 residue. Differences in hydrogen, sulfur, and nitrogen content were negligible. In general terms, the results of the elemental analysis of agave residues are in accordance with the characteristics of lignocellulosic biomasses.

Chemical composition analyzes revealed more relevant differences. The Hybrid Itaporanga agave residue presented a higher polysaccharide content (42.4%), while the Hybrid Bahia agave residue presented a lower polysaccharide content (31.4%). Due to its holocellulose and lignin contents (31% and 13.0%), Hybrid Itaporanga agave residue is a potential raw material for 2G bioethanol schemes. Extractives correspond to non-chemically bound substances from the lignocellulosic matrix. According to Barbosa et al. [25], substances such as waxes, saponins, resins, and phenols make up extractives from sisal samples. In the present study, the extractive contents were 23.2%, 33.4%, and 24.3% for Hybrid Itaporanga, Hybrid Bahia, and Mutant-1 agave residues, respectively. Extractive values are particularly high in plant samples (as in the present study) and are higher than in samples of agro-industrial residues, woods, barks, among others. In turn, the ash values in the present study were surprising. Satyanarayana et al. reported an ash content of only 5% in blue agave pomace [26]. In the present study, ash values were greater than 10%. Ash can act as a cracking catalyst in thermochemical processes (mainly alkaline earth metals). Although lignin levels are considered low ($\sim 12.5\%$), the high ash content in agave residues indicates that these biomasses are attractive for obtaining biochar (Allen & Downie, 2020). These ash contents also explain agave residues' low LHV and HHV values. The LHV results were in the range of $14.76\text{-}15.02 \text{ kJ} \cdot \text{kg}^{-1}$, while the HHV

results were in the range of 15.13-15.53 kJ.kg⁻¹. The negative effect of ash on the calorific potential of lignocellulosic biomass has already been reported in studies by Protásio et al. [27] and Belay et al. [28].

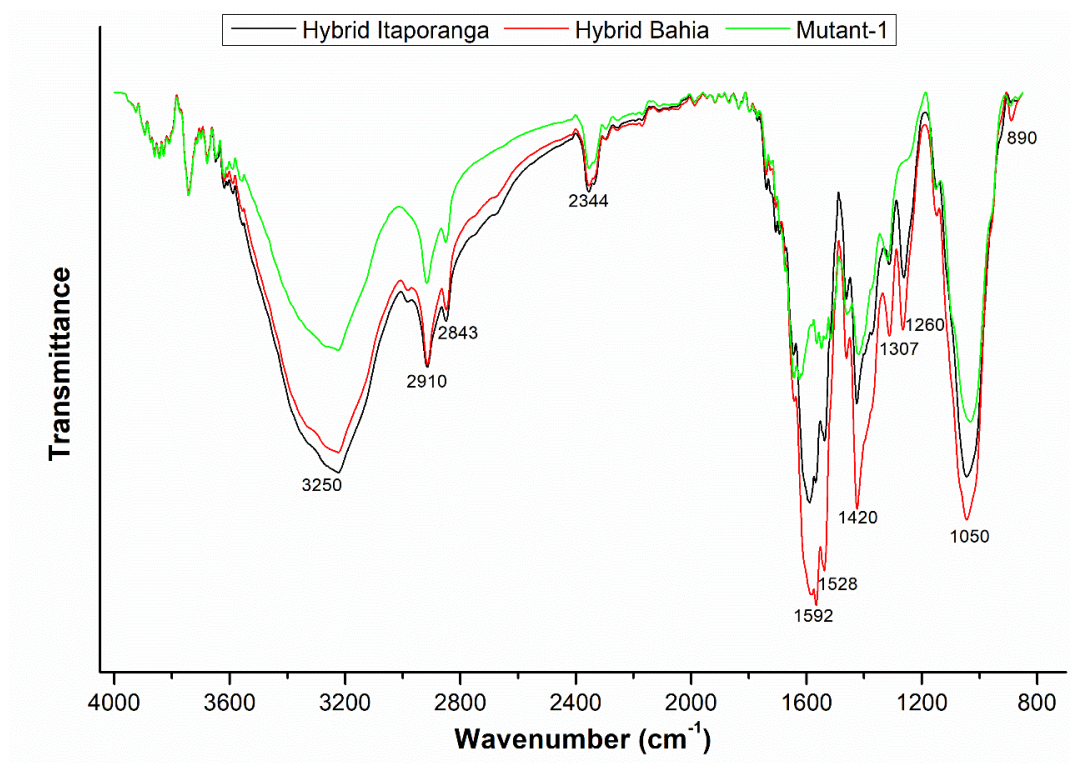
Table 1. Elemental content, heat of combustion and chemical characterization of agave residues.

Properties	Hybrid Itaporanga	Hybrid Bahia	Mutant-1
<i>Elementary content</i>			
C (%)	34.2 ± 0.10	35.2 ± 0.20	34.6 ± 0.30
H (%)	4.7 ± 0.00	4.9 ± 0.00	4.7 ± 0.00
O (%)*	46.6 ± 0.10	46.2 ± 0.20	47.1 ± 0.20
N (%)	1.2 ± 0.00	1.2 ± 0.00	1.2 ± 0.00
S (%)	0.2 ± 0.00	0.2 ± 0.00	0.3 ± 0.10
<i>Heat combustion</i>			
LHV (kJ.kg ⁻¹)	14.76	14.66	15.02
HHV (kJ.kg ⁻¹)	15.26	15.13	15.53
<i>Chemical composition</i>			
Moisture (%)	4.6 ± 0.20	5.7 ± 0.10	4.1 ± 0.10
Holocellulose (%)**	42.4 ± 1.10	31.4 ± 0.90	39.3 ± 0.50
Klason lignin (%)**	13.0 ± 0.00	13.2 ± 0.00	12.1 ± 0.00
Extractives (%)**	23.2 ± 0.10	33.4 ± 1.10	24.3 ± 0.60
Ash (%)**	12.1 ± 0.10	10.3 ± 0.20	13.9 ± 0.30

*The oxygen content was estimated by reducing the maximum content (100%) minus the carbon, hydrogen, nitrogen, and sulfur content. **The chemical composition was calculated from moisture-free biomass.

Figure 2 presents the transmittance profiles of agave residues in FTIR analysis. Peaks corresponding to OH stretching (3250 cm⁻¹), C-H stretching (2910 cm⁻¹), and CH₃ (asymmetric vibration) (2843 cm⁻¹) were common in all samples (Chowdhury et al., 2016). Peaks attributed to the bonds of cellulose (C-O stretching: 1050 cm⁻¹) and lignin (aromatic skeletal: 1592 cm⁻¹; CH₂ scissoring: 1420 cm⁻¹; C-O of syringyl ring: 1307 cm⁻¹) are also observed in the samples (Kurian et al., 2015) [29]. Subtle changes were observed in the peaks of phenyl ring (1528 cm⁻¹), C-O guaiacyl ring (1260 cm⁻¹) and C-H deformation in aromatic ring (890 cm⁻¹) [30]. Even though there were differences in holocellulose and extractive contents between agave residues, it was expected that the transmittance profiles would be similar. All samples come from the Agave sisalana; therefore, there were not sufficient changes in the S/G proportions of lignin or the accumulation of different substances in the extractives to promote relevant differences in the analysis.

Figure 2. Transmittance profile of agave waste samples of Hybrid Itaporanga, Bahia and Mutant-1.



The thermal degradation behavior of agave residues is shown in Figure 3. The first moments of the analysis (30-140 °C) promote the loss of free water from the samples. The main stage was established at 180-390 °C, which corresponds to a loss of 54% of the initial mass. Extractives are not chemically bound and are susceptible to thermal degradation [31]. This behavior was most evident with the Mutant-1 residue (Figure 2C), in which there is a degradation peak at 180 °C. In the other samples, the degradation of the extractives occurred at a higher temperature or probably in conjunction with hemicellulose, as in the analysis of the Hybrid Bahia residue (Figure 2B). In other words, the Hybrid Itaporanga agave residue presents more thermolabile extractives. After 300 °C, another degradation peak is well established, probably cellulose, according to Ferreira et al. [32]. At this stage, the degradation peaks of Hybrid Itaporanga, Hybrid Bahia, Mutant-1 agave residues occurred at temperatures of 340 and 460 and 680 °C, respectively. Degradation temperature differences were not observed in the following peaks (600 and 800 °C). This region is commonly attributed to lignin and confirms the structural similarity of the biopolymer between agave residues.

Figure 3. Mass loss profiles and differential thermal analysis (DTG) of the agave samples Hybrid Itaporanga (A), Hybrid Bahia (B), and Mutant-1 (C).

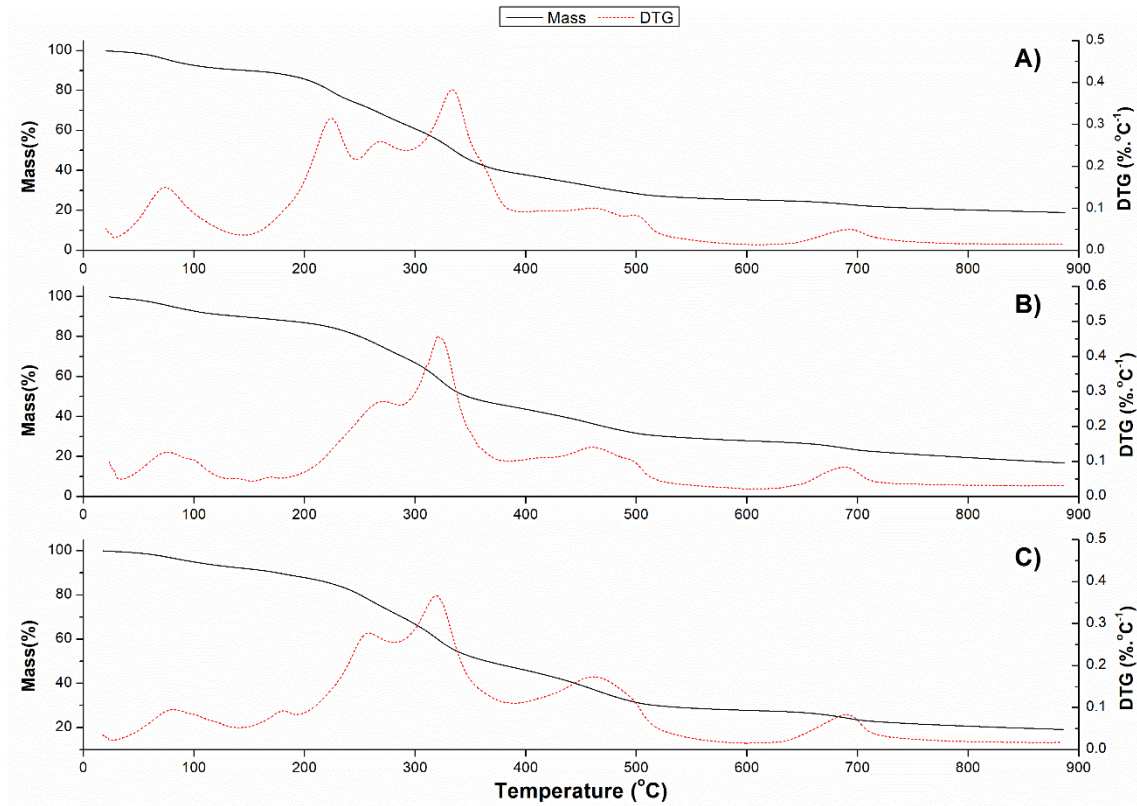


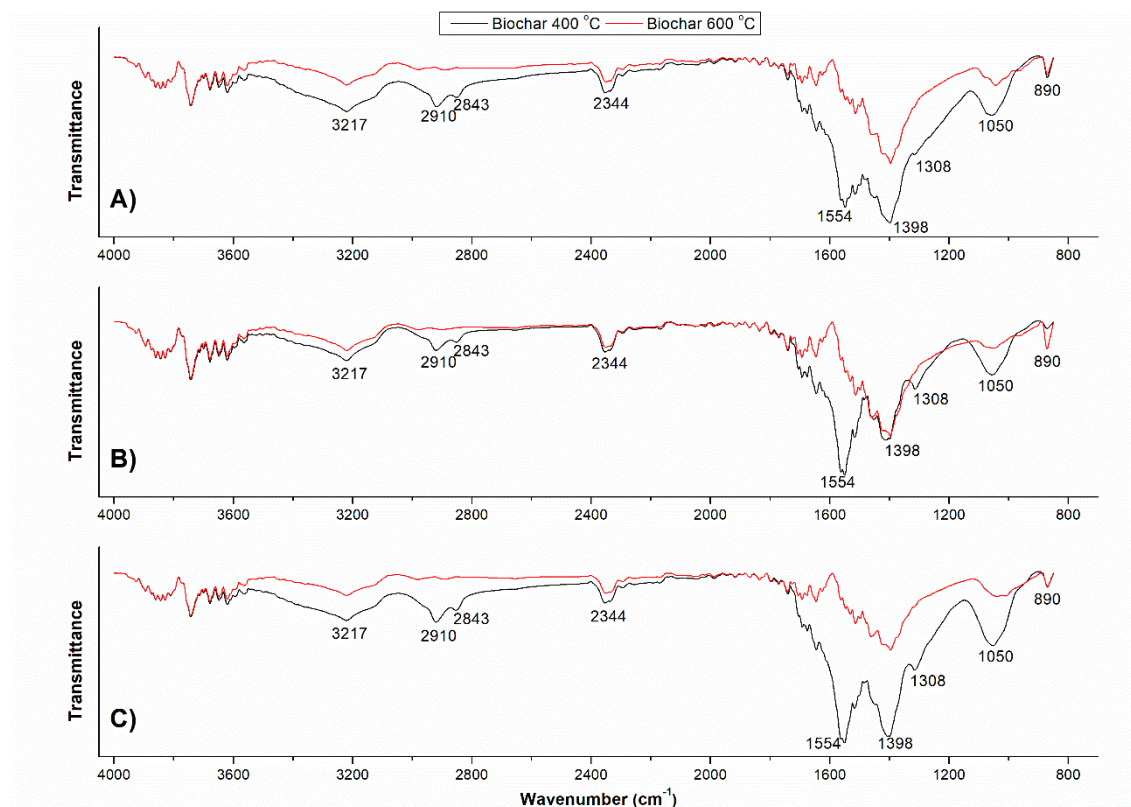
Table 2 shows the bio-oil and biochar yields from slow pyrolysis of agave waste. Increasing temperature led to reduced bio-oil yields but increased biochar yields. For example, in Hybrid Itaporanga residue pyrolysis, the yield increased from 22.2% to 35.7%, increasing the temperature from 400 to 800 °C. Maximum biochar yields from Hybrid Bahia and Mutant-1 residues were achieved at 600 °C. These samples were not tested in pyrolysis experiments at 800 °C. In fact, temperature is a critical factor in the slow pyrolysis process. The increase in temperature makes chemical bonds more susceptible to degradation and, consequently, implies greater degradation of solids. However, the opposite behavior was observed in the present study. These results can be attributed to the type of reactor used and the occurrence of recombination reactions [33].

Table 2. Bio-oil and biochar yield of agave samples under different temperatures in slow pyrolysis

Agave variety	400 °C		600 °C		800 °C	
	Bio-oil yield (%)	Biochar yield (%)	Bio-oil yield (%)	Biochar yield (%)	Bio-oil yield (%)	Biochar yield (%)
Hybrid Itaporanga	30.3 ± 0.8	22.2 ± 1.2	27.4 ± 0.9	32.5 ± 0.9	19.8 ± 0.2	35.7 ± 2.4
Hybrid Bahia	29.3 ± 0.7	28.6 ± 1.8	26.9 ± 1.0	32.3 ± 1.4	-	-

Figure 4 presents the transmittance profiles from the FTIR analysis of the biochar samples. The biochar generated during slow pyrolysis has a highly condensed polyaromatic structure due to successive disruption and recombination reactions. For this reason, temperature had a stronger impact on the chemistry of biochar than the type of agave waste used. The peaks corresponding to the stretching vibrations of the OH bond (3217 cm^{-1}), the C-H bond (1398 cm^{-1}), the C-O bond (1050 cm^{-1}), and the C=C bond (890 cm^{-1}) were common in the biochar obtained at 400 and 600 °C [34]. However, differences were recorded between the samples at 2910 and 2843 cm^{-1} , corresponding to the vibration of the C-H bonds of aliphatic moieties. This result confirms the absence of aliphatic portions in samples obtained at 600 °C, indicating that these biochar' structure is more aromatic. This behavior was also recorded by Yang et al. (2021) [35] in studies to obtain biochar at different temperatures. The greater aromatization of biochar with increasing temperature was also confirmed by observing the peak of 1554 cm^{-1} (C=C stretching), which was only evident in biochar obtained at 400 °C. The peak corresponding to the C-OH bond (1308 cm^{-1}) (El-Maghrabi et al., 2021) occurs in samples at 400 °C but is non-existent in samples at 600 °C. This result indicates that biochar obtained at 400 °C still have more active oxygen functional groups than biochar obtained at 600 °C.

Figure 4. Transmittance profile of biochar samples from agave residues of the Hybrid Itaporanga (A), Hybrid Bahia (B), and Mutant-1 (C) varieties.



Structural analyzes were carried out to evaluate other effects of temperature on biochar. At this stage, only Hybrid Itaporanga residue was used as raw material for biochar. The results of surface area, micropore volume, and pore size are shown in Table 3. Table S1 presents the percentages of elements contained in the biochar. The increase in temperature promoted an increase in the surface area of Hybrid

Itaporanga waste biochar. Increasing the temperature from 400 to 800 increased the surface area by more than 14 times. Micropore volume values increased strongly with increasing temperature used in pyrolysis. The micropore volumes were 5.89×10^4 , 13.53×10^4 , and $73.08 \times 10^4 \text{ cm}^3.\text{g}^{-1}$ at temperatures of 400, 600, and 800 °C, respectively. Increasing temperature implies a greater extent of lignin degradation, so more volatile compounds are released and, consequently, more micropores are opened (Wong et al., 2019). Pore size showed another behavior. Biochar obtained at 400 and 600 °C were 549.6 and 622.1 Å, while biochar from 800 °C were 142.1 Å in size. Despite the increase in surface area, the reduction in pore size is not desirable for dye adsorption. According to Jung et al. (2017), the predominance of mesopores favors the dye adsorption on biochar.

Table 3. Physical properties of biochar samples from Hybrid Itaporanga agave residue obtained at temperatures of 400 (I400), 600 (I600), and 800 °C (I800).

Type of bio-char	BET surface area ($\text{m}^2.\text{g}^{-1}$)	Micropore volume ($\text{cm}^3.\text{g}^{-1}$)	Average adsorption pore diameter (Å)
I400	2.87	5.89×10^4	549.6
I600	1.79	13.53×10^4	622.1
I800	40.58	73.08×10^4	142.1

MB dye adsorption equilibrium data on biochar obtained at 400 and 600 °C are presented in Figure and Table 4. As expected, the increase in the MB dye concentration in the liquid phase favored the increase in the adsorption capacity of the biochar. Experiments with biochar at 400 °C showed an adsorption capacity of 35 mg.g^{-1} with complete removal of MB dye from the liquid phase, and then the adsorption capacity grew slowly, exceeding 80 mg.g^{-1} . In turn, the biochar obtained at 600 °C showed a maximum adsorption capacity of 40 mg.g^{-1} . The decline in adsorption capacity in biochar obtained at 600 °C can be explained by the loss of functional groups with active oxygen (hydroxyl, phenols, carboxylic acid, among others) during pyrolysis. These functional groups are susceptible to ionization at alkaline pHs, and they are sites for ion exchange with the cationic dye. Suhaimi et al. (2022) also reported that biochar obtained at 600 and 800 °C were worse for MB dye adsorption than biochar obtained at 500 °C [36], [37].

Regardless of agave residue and temperature, the Freundlich model ($R^2 = 0.95\text{-}0.99$) was more efficient in describing equilibrium data than the Langmuir model ($R^2 = 0.85\text{-}0.96$). The Freundlich coefficients of the 400 °C biochar were higher than those of the 600 °C biochar. Unfortunately, screening the best raw material for biochar is not yet possible, since the n values also varied among the agave residues. To prospect for biochar with better performance, only biochar obtained at a temperature of 400 °C were used in the following steps.

Figure 5. Methylene blue adsorption isotherms on biochar obtained from agave waste. The biochar were prepared by slow pyrolysis at 400 and 600 °C with agave residues from the Hybrid Itaporanga (A), Hybrid Bahia (B) and Mutant-1 (C) varieties.

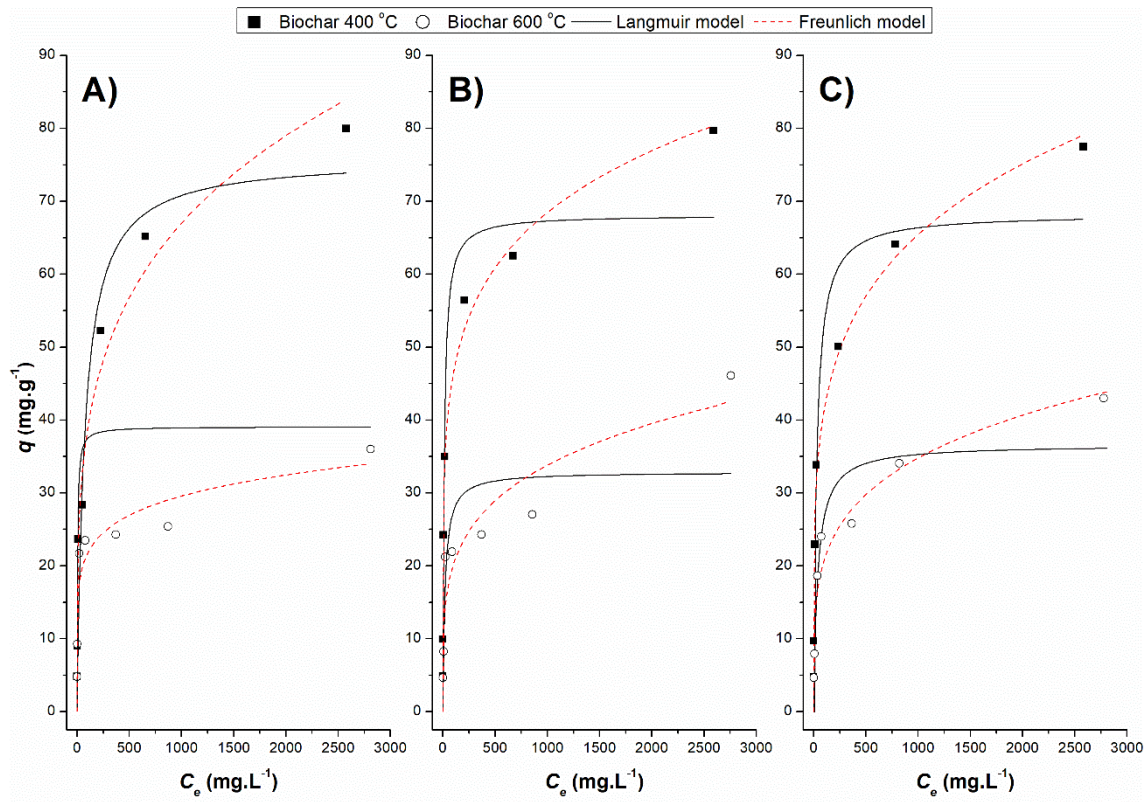


Table 4. Parameters of the Langmuir and Freundlich models corresponding to the MB dye adsorption equilibrium tests on agave residue biochar. I400 and I600: Hybrid Itaporanga obtained at 400 and 600 °C; B400 and B600: Hybrid Bahia obtained at 400 and 600 °C; M400 and M600: Mutant-1 obtained at 400 and 600 °C.

<i>Langmuir</i>						
	I400	I600	B400	B600	M400	M600
$q_{\max}$ (mg.g ⁻¹)	75.9 ± 7.6	39.1 ± 3.3	68.1 ± 5.6	32.9 ± 4.7	68.2 ± 0.7	36.6 ± 3.3
k_d (L.mg ⁻¹)	72.8 ± 34.7	4.3 ± 2.6	12.5 ± 5.8	19.7 ± 5.6	28.4 ± 0.1	37.7 ± 16.7
R^2	0.96	0.91	0.96	0.85	0.96	0.94
<i>Freundlich</i>						
	I400	I600	B400	B600	M400	M600
K (mg ^{1-1/n} .L ^{1/n} .g ⁻¹)	12.9 ± 2.4	11.7 ± 2.6	21.4 ± 3.5	7.2 ± 2.1	16.5 ± 3.1	7.4 ± 1.4
n	4.2 ± 0.5	7.4 ± 1.9	5.9 ± 0.9	4.5 ± 0.9	5.0 ± 0.7	4.4 ± 0.6
R^2	0.98	0.95	0.99	0.99	0.98	0.97

Adsorption kinetics of MB dye onto biochar are shown in Figure 6. The effectiveness of biochar to remove dyes from the liquid phase was already evident in the first moments. MB dye removal after 1 min reached 60% ($C/C_0 = 0.4$) and 20% ($C/C_0 = 0.8$) in experiments with initial concentrations of 100 and 250 mg.L⁻¹, respectively. Then, the dye concentration in the liquid phase decreases until equilibrium. Due to the lower solute content, the decline of MB dye in the liquid phase was more abrupt in experiments with an initial MB dye concentration of 100 mg.L⁻¹. The kinetic experiments also allowed us to identify the biochar with the greatest potential to remove MB dye, the biochar obtained from the Hybrid Itaporanga residue. Using this biochar, experiments with 100 mg.L⁻¹ reached equilibrium at 10 min and showed 95% removal of MB dye after 120 min in experiments with an initial solute concentration of 250 mg.L⁻¹. The other biochar performed worse. The biochar obtained from the Mutant-1 residue no longer ensured complete dye removal in experiments with an initial concentration of 100 mg.L⁻¹. In turn, Hybrid Bahia waste biochar removed only 80% of MB dye after 120 min.

Table 5. Parameters of the pseudo first-order and pseudo-second-order models on the adsorption kinetics of MB dye on biochar. I400-Biochar from Hybrid Itaporanga obtained at 400 °C; B400 – Biochar from Hybrid Bahia obtained at 400 °C; M400-Mutant 1 Biochar obtained at 400 °C.

Adsorption kinetics data	I400	B400	M400
Pseudo-first-order constant – K_1 (MB dye = 100 mg.L ⁻¹)	0.014	0.020	0.016
R^2	0.15	0.61	0.53
Pseudo-first-order constant – K_1 (MB dye = 250 mg.L ⁻¹)	0.028	0.025	0.029
R^2	0.94	0.85	0.97
Pseudo-second-order constant – K_2 (MB dye = 100 mg.L ⁻¹)	0.052	0.051	0.051
R^2	1.00	1.00	1.00
Pseudo-second-order constant – K_2 (MB dye = 250 mg.L ⁻¹)	0.021	0.028	0.023
R^2	0.98	0.90	0.99

Table 5 presents the parameter values of the pseudo-first-order and pseudo-second-order models to fit the adsorption kinetic data. Regardless of the initial solute concentration and the type of biochar, the pseudo-second-order model was more efficient. For example, in the condition with 100 mg.L⁻¹ MB dye and Mutant-1 biochar, the pseudo-second-order model presented an R^2 value equal to 1.00. In contrast, the pseudo-first-order model only obtained R^2 equal to 0.53. The pseudo-second-order model is more suitable for situations where chemisorption is rate limiting, and it is widely applied in dye removal studies from biochar [38],[39].

Figure 6. MB dye adsorption kinetics on agave residue biochar from Hybrid Itaporanga (A), Hybrid Bahia (B), and Mutant-1 (C). The experiments were carried out with 0.5% (w/v) biochar, pH 9.0, and 150 rpm.

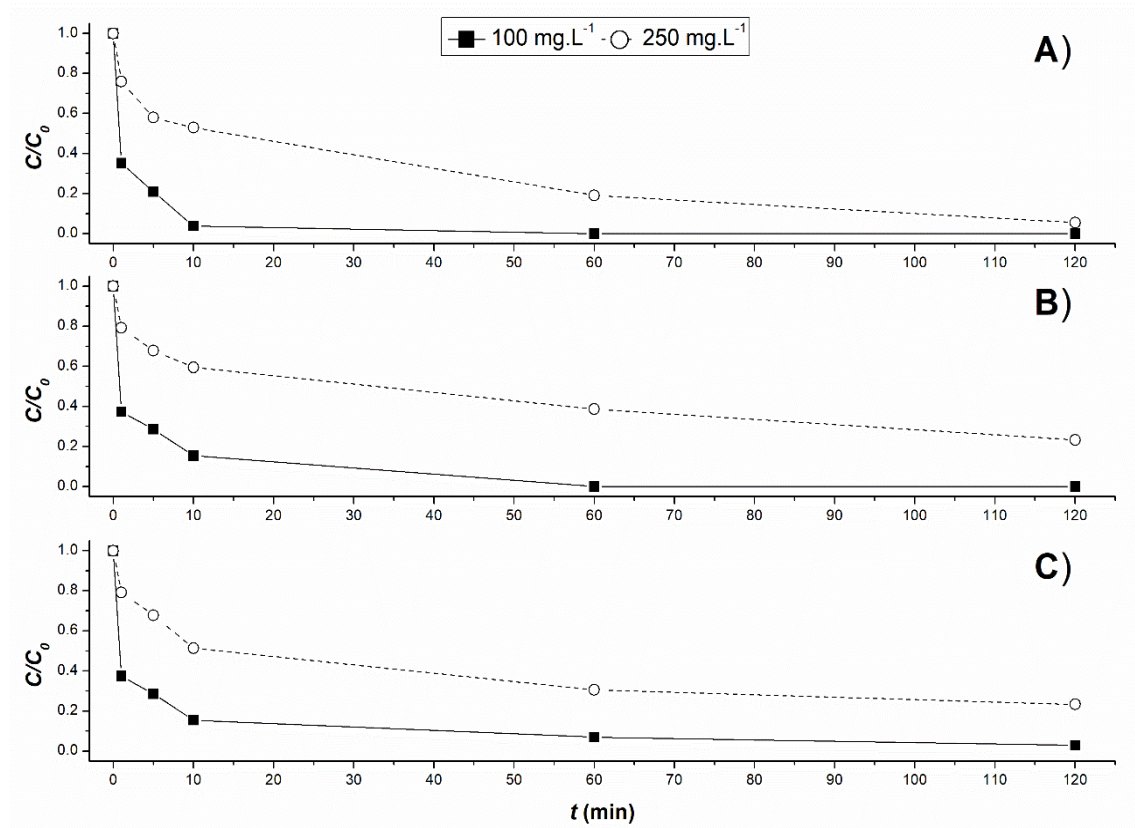


Figure 7 shows the MB dye adsorption in a fixed bed column with agave residue biochar. All curves showed an S-shape, which is characteristic of the dynamic nature of the experiment. The injected dye is eventually captured during the passage of the bed in the first moments of the experiment so that the presence of dye at the column exit occurs after saturation of the initial layers of the fixed bed. In the present study, experiments with biochar from Hybrid Itaporanga (I400) and Hybrid Bahia (B400) residues showed non-zero concentrations of MB dye after 60 and 40 mL, respectively. Mutant-1 residue biochar showed lower performance due to the presence of MB dye at the column exit already at 10 mL of flow and the displacement of its data to the left. The continuous injection of dye into the fixed beds increased the dye concentration in the liquid phase to $C/C_0 = 0.85$ (equivalent to 212.5 mg.L⁻¹) for the Hybrid Bahia and Mutant-1 biochar. In comparison, the solute concentration only reached $C/C_0=0.63$ (equivalent to 157.5 mg.L⁻¹) for Hybrid Itaporanga biochar. This behavior corroborates the better performance of Hybrid Itaporanga waste biochar over other biochar. In experiments with Hybrid Itaporanga residue, the dye injection was left beyond 200 mL of solution to reach saturation, but the dye concentration in the liquid phase increased little. DAC values reached 179, 123, and 75 mg.g⁻¹ for Hybrid Itaporanga, Hybrid Bahia, and Mutant-1 biochar, respectively. DAC values with other results in the literature are illustrated in Table 6.

Figure 7. Dynamic MB dye adsorption in a fixed bed column filled with biochar from Hybrid Itaporanga (I400), Hybrid Bahia (B400), and Mutant-1 (M400). Biochar were produced by slow pyrolysis at 400 °C for 1 h. The adsorption experiments were carried out with an initial MB dye concentration of 250 mg. L⁻¹ and a bed height of 6 cm (equivalent to g).

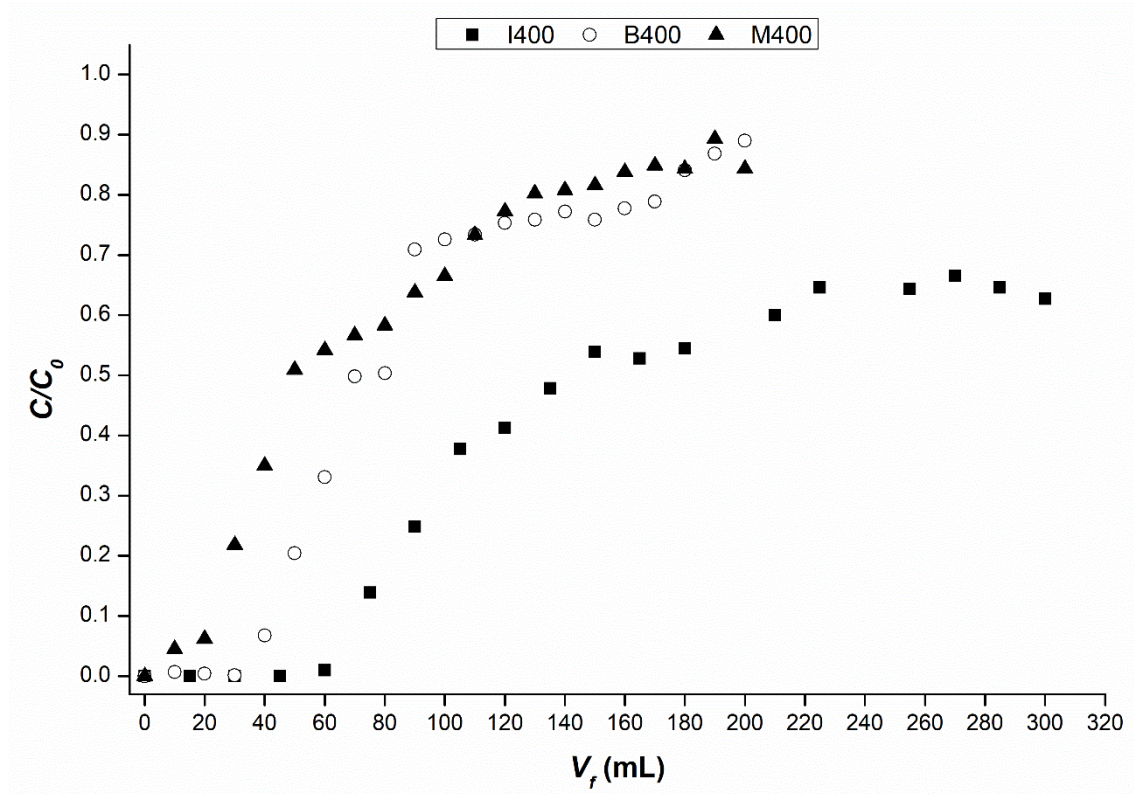


Table 6. Dynamic adsorption capacities (DAC) of methylene blue column adsorption with biochar

Biochar (raw material and pyrolysis condition)	Column adsorption conditions	BET surface area (m ² .g ⁻¹)	Dynamic adsorption capacity (mg g ⁻¹)	References
Sugarcane bagasse pyrolyzed at 500 °C	40 mg L ⁻¹ MB dye, 10 cm bed height	322.96	31.10	[40]
Tea powder pyrolyzed at 700 °C (NaOH activation)	50 mg L ⁻¹ MB dye	441.00	79.59	[41]
Pine corn pyrolyzed biochar	50 mg L ⁻¹ MB dye, 7 cm kaolin bed height	335.00	20.25	[42]
Egg shell membrane pyrolyzed biochar at 700 °C	100 mg L ⁻¹ MB dye	8.48	101.10	[43]

Lychee seed pyro- lyzed at 700 °C (KOH activation)	100 mg L ⁻¹ MB dye	154.00	124.50	[38]
Rice straw pyro- lyzed at 700 °C (HCl activation)	50 mg L ⁻¹ MB dye	378.02	67.00	[39]
Agave residue py- rolyzed at 400°C (HCl activation)	50 mg L ⁻¹ MB dye, 6 cm bed height	2.87	179.76	This work

As illustrated in table 6, the DACs of various adsorption experiments for MB dye removal were investigated. The biochar tea powder had the highest BET surface area of 441 m².g⁻¹ at 700 °C while the agave residue surface area was 2,87 m².g⁻¹ obtained at 400 °C. This disparity in surface area can be attributed to the pyrolysis temperatures used to obtain the biochar. At higher temperatures, higher value of BET surface area is obtained generally for biomass pyrolysis [44], [45]. Nonetheless, the HCl activated agave biochar showed an excellent DAC value (179 mg.g⁻¹) compared to the rest of the biochar obtained, as the activation improves its adsorption capacity. Furthermore, from the BET analysis, agave biochar showed a macropore characteristic, which is good for removal of contaminants made of bigger molecules such as MB dye [41].

Conclusions

In general, the agave varieties showed similar chemical characteristics. All agave residues presented low combustion responses (HHV of 15 MJ/kg), possibly due to the high ash content. Changing the agave variety resulted in more significant changes in the content of extractives and holocellulose. The increase in temperature surprisingly increased the biochar yields and the surface area of the product, but the biochar generated at higher temperatures showed low adsorption capacity for MB dye. No effect of agave variety was observed on biochar yield and chemistry. FTIR analyses showed the loss of functional groups in biochar obtained at 600 °C compared to biochar obtained at 400 °C. Hybrid Itaporanga residue biochar obtained at 400 °C stood out from other biochar due to its MB dye adsorption performance in batch and column tests.

Statements and Declarations

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