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Production and application of activated carbon obtained from the thermochemical degradation of corn cob

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Abstract: The present work aims to perform the thermal degradation of corn cobs to produce activated carbon, which is used in a column adsorption system for the dechlorination of supply water. The biomass under study and the product generated by pyrolysis in a fixed bed reactor were analyzed using classical methods (moisture, volatile materials, ash and fixed carbon, lignin, cellulose, hemicellulose, and apparent density) and instrumental methods (thermogravimetry and CNH). In the pyrolysis process, the following parameters were studied: temperature (360 to 640 oC) and heating rate (13 to 27 oC/min). The reaction time was 30 minutes. The dechlorination test using the activated carbon obtained in this research was conducted in an adsorption column in continuous flow at an average flow rate of 6 mL/min. The iodine number of adsorbent produced in this research was calculated. The results obtained showed that the carbon content (44%) and the lignin content (28%) point to the use of residual biomass studied in this research to produce activated carbon via the thermal route. The highest activated carbon yield was 71.12% at a temperature of 360 °C with a heating rate of 20 °C/min. While the minimum yield was 21.6% with a temperature of 600 °C and a heating rate of 25 °C/min. The iodine number of the activated carbon produced at 640 oC was 820 mgI2/g. In the adsorption test, the following coefficients from the Thomas model were obtained: kTH = 0.0093 mL/mg.min and qo = 98 mg/g, when a liquid flow equal to 9.9 mL/min was used. The adsorption capacity of coal is related to the flow rate of the dye solution, being noticed that the higher the liquid flow rate in the column, the higher the adsorbate mass transfer coefficient.

Keywords: Biomass, agricultural waste, pyrolysis, adsorption, Thomas model

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1. Introduction

Biomass is defined as all organic material of plant origin, which, through the process of photosynthesis, can store the sun's radiant energy in its chemical composition, to later be converted into other forms of energy. The energy present in its components can be transformed through physical, chemical, and biological conversion processes into liquid, solid and gaseous fuels, aiming to increase the economic efficiency of the product (Duong et al., 2019; Paz et al., 2023; Pedroza et al., 2014; Pedroza, Neves et al., 2021).

Corn is one of the main crops highlighted in Brazil. In an interval of 140 days, a seed of approximately 0.3 g produces about 1.2 kg of biomass. Although they have a high productive potential, the resulting waste is not used on a large scale for energy generation (Zambrzycki et al., 2014).

According to a survey conducted by United States Department of Agriculture (United States Department of Agriculture, 2017), the corn crop from the second half of 2017 to the first half of 2018 in Brazil will produce approximately 95 million tons of corn, a decrease of 0.5% in compared to the previous crop. Despite the significant drop in production, the data demonstrate the significant importance of cereal production in the country.

The generation of waste for each ton of corn harvested is 2.3 tons. Such residues comprise the culm, straw, cob, and corn leaves (Júnior et al., 2021). Considering the relationship presented by the authors and the data pointed out by the USDA (United States Department of Agriculture, 2017), for the 2017/2018 harvest, approximately 218 tons of corn residues would be generated.

In Brazil, corn is the second most produced grain. In the 2021 harvest, around 107.8 million tons of this cereal were harvested. However, for each ton of maize harvested, approximately 1.96 tons of waste are generated, including stalk, leaves, cob, and straw. These residues are subject to treatment and can be used for alternatives such as: composting, energy generation and to obtain activated carbon (Martins-Vieira et al., 2023).

In view of the problems caused by the incorrect destination of these residues, several researchers study techniques and methods that aim to solve such adverse effects, thus aiming at an environmentally correct and safe destination for residues from corn production (Cao et al., 2004; Daioglou et al., 2016; Klaas et al., 2020; Singh & Sawarkar, 2020).

The conversion of biomass into bioproducts is conducted using two main process technologies: thermochemical and biochemical. Pyrolysis represents one of the main thermochemical methods, where biomass is converted into bioproducts with a higher added value than the initial one (bio-oil, activated carbon, acid extract and biogas). In this way, the application of the thermochemical degradation process in the residues generated in the corn crop, aiming at their final destination, shows up as an important study to be developed and an important alternative to use and add value to production chains (Alavijeh & Yaghmaei, 2016; Ceranic et al., 2016; Kirubakaran et al., 2009; Pedroza, da Silva et al., 2021).

This work aims to conduct the thermal degradation of residues from corn production, and subsequently use the adsorbent obtained in a methylene blue dye adsorption column, with the obtained experimental data adjusted to the Thomas model.

2. Materials and methods

2.1. Waste collection and sample preparation

The residue used in the present work is fresh corn cob from the industrial processing of corn (Zea mays L). All residues used for analysis and experiments were collected at the Paraíso farm, located in Paraíso city (Tocantins), in the Amazon region of Brazil. The residues were dried at 60 °C in an oven for a period of 24 hours (Figure 1).

Figure 1. Drying of biomass.

To promote the homogeneity of the biomass and facilitate the analytical procedures, all samples were ground in a knife mill, Trapp, model Trf-300, 3.0Cv – Bivolt (Figure 2).

Figure 2. Biomass crushing for tests.

After the grinding process, the residue was sieved in a sieve with an opening of 1.41 mm (ABNT, Mesh 14). The immediate analysis of the material was made by the following methods: moisture (ISO-589-1981), ash (ISO-1171-1976), volatile material (ISO-5623-1974) and fixed carbon (obtained by difference). The Klason method was used to determine the cellulose, hemicellulose and lignin contents of the studied biomass, and the components were extracted in 03 steps, using the solvents neutral detergent, acid detergent and 72% H_2SO_4.

2.2. Instrumental analysis of biomass

Corn cob samples were evaluated through the ignition method in a Perkin-Elmer CHNS/O 2400 series II elemental analyzer, for the determination of carbon, hydrogen, and nitrogen contents. Thermogravimetric characterization was performed on the material with heating rates of 10 and 30 °C/min in the Thermogravimetric analyzer equipment Shimadzu, model TGA-50.

2.3. Preparation of corn cob briquettes and pyrolysis tests

The briquettes were produced from a biomass volume of 320 mL of corn cob, previously dried and with a granulometry of 1.41 mm. Subsequently, approximately 70 mL of distilled water was added to this material for hydration. The biomass remained at rest for 30 minutes. Afterwards, the hydrated material was pressed inside a 20 cm long and 32 mm diameter pipe. The briquettes obtained were dried in an oven at 40 °C for a period of 24 hours (Figure 3).

Figure 3. Briquettes obtained from the cob of corn.

The thermal conversion was conducted in a fixed bed reactor with a length of 100 cm and an external diameter of 10 cm (Figure 4). Biomass was introduced to the reactor in the form of briquettes. The reactor was heated through a split oven. The reactor was operated in batch mode, using heated water steam as the carrier gas. The steam flow was fixed in all tests (8 mL/min).

A thermocouple was coupled to the reactor, aiming at monitoring the temperature inside the bed. The temperature range and heating rate used in the pyrolysis plant ranged from 360 to 640 °C and from 13 to 27 $^{o}C.min^{-1}$, respectively. The reaction time will be fixed at 30 minutes.

Figure 4. Pyrolysis reactor used in the tests.

At the outlet end of the reactor, a condensation system was inserted to recover the produced liquids. activated carbon was removed from the reactor after the material had cooled.

2.4. Iodine number and adsorption column test

The iodine number of activated carbon was determined through ASTM D4607-94.

To investigate the industrial application of the activated carbon obtained, removal of the methylene blue dye was conducted in an adsorption column using the activated carbon produced in this research.

The system consisted of the following components: (a) raw water reservoir, (b) peristaltic pump, (c) raw wastewater agitator-motor and (e) activated carbon filter. The transport of liquids was performed by silicone tubing (Figure 5).

Figure 5. Adsorption tests.

The raw wastewater tank has a capacity of 100 liters. The agitator motor aims to distribute the methylene blue dye in raw water. The feeding of the adsorption column was controlled by the programmable flow of the peristaltic pump, which allowed evaluating the efficiency of the system through the flow of raw effluent. In this research, the effect of flow on the dye adsorption process was studied, with two values of liquid flow being evaluated (5.1 and 9.9 mL/min).

The adsorption columns were manufactured from a PVC pipe with a diameter of 20 mm and a length of 12 cm. During the tests, a mass of 6 grams of activated carbon was used in each experiment.

The experimental data in the adsorption test was fitted to the Thomas model, which is used in mathematical modeling of the adsorption process in continuous systems, such as a fixed bed, to analyze laboratory scale column data and provide a prediction of the rupture curve.

Thomas model allows determining the maximum adsorption capacity of the fixed bed, as well as the rate at which adsorption occurs (Equation 1).

$$\ln\left(\frac{Co}{Cx}-1\right)=\frac{KTH.qe}{Q}-KTH.Co.t \qquad (1)$$

Where Co (mg/L) is the adsorbate concentration in the input feed solution; Cx (mg/L) is the adsorbate concentration at the bed outlet; KTH (L/(min.mg) is Thomas's kinetic constant; qe is the maximum adsorption capacity of the adsorbent; Q (mL/min) is the bed feed volumetric flow rate; w (g) is the mass of adsorbent and t (min) is the operating time of the system.

3. Results and discussion

3.1. Biomass characterization

The results obtained through the immediate and elementary analyzes shown in Table 1. Where: SM: corn cob, PD: tree pruning, BC: sugarcane bagasse and FC: coconut fiber.

The moisture content of the biomass was 9.14%. The moisture content of materials plays a key role in the development of pyrolysis. This can be confirmed by the fact that pyrolysis is less drastic when the process is conducted with dry matter (Pedroza et al., 2014). In this case, the pyrolysis products have slightly decomposed components, especially oxygenated compounds. According to some researchers (Paz et al., 2023; Bridgwater, 2012), the water content has an important impact on the energy consumption for biomass drying.

The ash content refers to the percentage of inorganic compounds present in the biomass, such as potassium, magnesium, iron, calcium, sodium, phosphorus, among others. In the determination of ash, the biomass is submitted to a combustion process at temperatures in the range of 710 ºC, where the organic components react with oxygen in the process, leaving only the inorganic minerals. In this work, the ash content obtained was of the order of 1.98%. Pedroza et al. (2022) determined that ash content has a major influence on the pyrolysis of biomass. According to the authors, the ash content of the biomass favors an increase in the yield of the gaseous fraction and a decrease in the percentage of the liquid fraction, under the operational conditions studied (fluidized bed reactor, bed temperature of 550 ºC, nitrogen gas carrier).

The volatile material content is related to the loss, in mass, of components that volatilize at temperatures close to 900 ºC. Unlike ash content, volatile mass is determined in an inert atmosphere, in the absence of oxygen. The higher the content of volatile materials, the greater the power of reactivity of the biomass, as it is linked to the ignition power of the material. In this research, the content of volatile material found was 88.12%. The content of volatile material in the biomass directly interferes with the biomass burning process. The higher the volatile content, the greater the reactivity and consequently the ignition (Bridgwater, 2012).

Fixed carbon comprises the percentage of compounds remaining after the process of releasing volatile materials, removing ash and moisture. The fixed carbon content of corn cob biomass was 9.90%, a value close to those obtained by Alves et al. (2016). For these authors, there are significant positive correlations between the parameter's lignin content and fixed carbon content in the biomass. The highest yield of fixed carbon can be found for samples with higher lignin contents, and this is explained by the fact that this fundamental component of wood is more resistant to thermal decomposition when compared to cellulose and hemicellulose, due to its complex structure.

Table 1. Results of immediate analysis from different biomasses.

Biomass	Moisture (%)	Volatile material (%)	Ash (%)	Fixed carbon (%)	Researchers
SM	9.14	88.12	1.98	9.90	This research
SM	9.62	87.47	2.51	10.02	Alves et al. (2016).
PD	8.63	70.95	20.23	8.80	Pedroza, Neves et al. (2021).
FC	8.87	84.11	1.99	13.90	Paz et al. (2023).

The percentages of carbon, hydrogen, nitrogen, oxygen, and sulfur present in the corn cob biomass are presented in Table 2. The carbon content present in biomass studied by e Paula et al. (2011). The C/H ratio in the biomass studied here was 6.7. A relationship of significant importance in the process of carbonization of biomass is the C/H ratio, which tends to have a higher absolute value in activated carbon when compared to biomass, due to greater aromatization and chemical change. of material (Soares et al., 2014). Vassilev et al. (2010) report that biomass is normally rich in moisture, volatile compounds, Ca, Cl, H, K, Mg, Mn, Na, O and P and has a lower content of ash, fixed carbon, Al, Fe, N, Si, S and Ti, when compared with the activated carbon obtained in the pyrolysis.

Lignocellulosic materials are present in the chemical structure of biomass. Cellulose, hemicellulose, and lignin contents of the corn cob are shown in Table 3.

The chemical composition of the biomass varies according to the species and the place of cultivation. According to the researchers, the contents on a dry basis can reach between 40 and 55% of cellulose, from 25 to 50% of hemicellulose and between 15 and 35% of lignin (Manzato et al., 2017). The results of the present research fall within the ranges of contents found by the author. The lignin content in the in natura biomass of this research was approximately 28% and it contributes to the chemical characteristics of the bio-oil produced in the biomass pyrolysis process as well as to the activated carbon properties. Lignin is an aromatic macromolecule, highly irregular in its amorphous constitution, with an elemental composition of carbon, hydrogen, and oxygen (Paz et al., 2023). It is a complex polymer responsible for the formation of the cell wall that has a high molecular weight and as a structural base phenyl-propane units and is linked to the Polysaccharides (polyoses) of wood.

Figure 6 shows thermal decomposition data of lignocellulosic compounds in corn cob biomass.

Four major mass loss events were identified in the analysis. The initial and final temperatures of each event are shown in Table 4. According to Figure 6, the reduction of humidity is observed through two events, the first is indicated at 38 °C and the following is observed around 155 °C. In these two events, it is noticed the loss of water and other liquids that volatilize in this temperature range. On the other hand, the temperature where the second event is found is much higher than the boiling point of water, and this is explained by the fact that materials with a high percentage of ash in their chemical composition have maximum release of volatiles at higher temperatures (Chiaramonti et al., 2007; Conesa et al., 2009). In sequence, another considerable loss in the percentage of mass is noticed, between the temperatures of about 150 to 220 °C, referring to the thermal decomposition of the hemicellulose, considering that in thermal processes, this fraction is the first that suffers alteration in its chemical structure. The third major loss is due to the decomposition of cellulose, which occurred between the ranges of 245 to 360 °C. Finishing the chemical degradation, there is lignin, which starts around 400 °C and remains until 900 °C, ending the loss of mass.

3.2. Activated carbon yields obtained during corn cob pyrolysis

The experimental results obtained in the multivariable factorial experimental design (central composite rotational design - CCRD) are shown in Table 5. In this design, the following factors were investigated: reactor temperature (°C) and heating rate (°C/min). To determine the experimental error of the experimental design used in this research, in experiments 5, 6 and 7 the same conditions were used for the two factors used (temperature = 500 °C and heating rate = 20 °C/min).

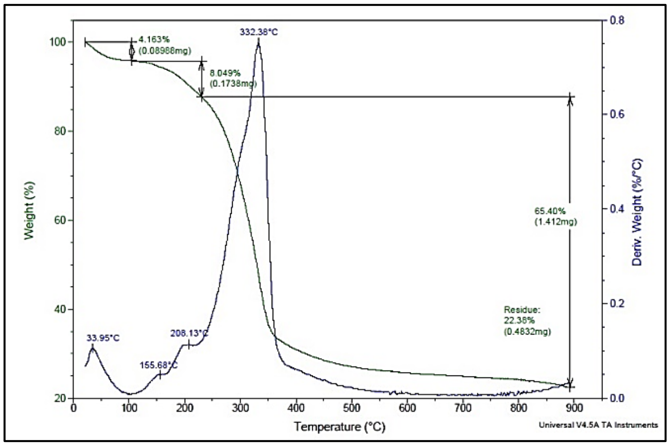

Figure 6. Thermogravimetric degradation curve of corn cob biomass.

Table 2. Results of elemental analysis of biomass.

Elements					Researchers
C (%)	N (%)	H (%)	O (%)	S (%)	
43.81	1.27	6.53	48.39	-	This research
45.50	0.50	6.70	47.00	0.30	e Paula et al. (2011).
46.20	0.92	5.42	47.22	0.24	Danish et al. (2015).

Table 3. Lignocellulosic composition of corn cob.

Lignin (%)	Cellulose (%)	Hemicellulose (%)	Researchers
27.93	50.20	24.00	This research
21.03	40.65	41.15	Pedroza, Neves et al. (2021).
21.07	26.20	25.80	Paz et al. (2023).

Table 4. Thermogravimetric curves of corn cob biomass.

Event	Initial temperature (ºC)	Final temperature (ºC)	Initial mass (mg)	Final mass (mg)	Mass loss (%)
1	20	115	2.159	2.069	4.16
2	150	220	2.069	1.895	8.04
3	245	360	1.895	1.209	36.20
4	400	900	1.209	0.953	21.16

Table 5. CCRD planning results.

Experiments	Variables		Carbon yield (%)
	Temperature (ºC)	Heating rate (ºC/min)	
1	- (400)	- (15)	36.45
2	+ (600)	- (15)	28.02
3	- (400)	+ (25)	46.89
4	+ (600)	+ (25)	21.61
5	0 (500)	0 (20)	28.19
6	0 (500)	0 (20)	28.10
7	0 (500)	0 (20)	28.14
8	-1,4 (360)	0 (20)	71.12
9	0 (500)	1,4 (27)	25.84
10	1,4 (640)	0 (20)	24.22
11	0 (500)	-1,4 (13)	25.12

The highest activated carbon yield was 71.12% at a temperature of 360 °C with a heating rate of 20 °C/min and a pyrolysis time of 30 minutes. While the minimum yield was 21.6% with a temperature of 600 °C and a heating rate of 25 °C/min.

Figure 7 shows the Pareto diagram obtained from the experimental data and the influence of the parameters studied on activated carbon production.

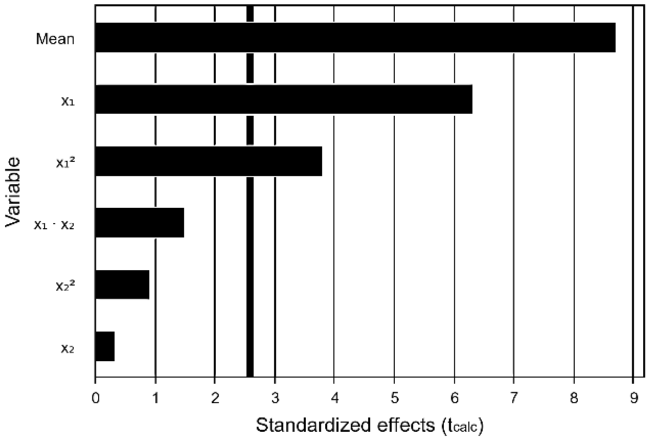

Figure 7. Pareto diagram obtained from the CCRD planning.

The Pareto diagram (Figure 7) generated from the DCCR factorial design data showed that temperature had a negative effect on activated carbon production (-6.29). The heating rate had no significant effect at a 95% confidence level.

The final temperature of pyrolysis plays a significant role in the various chemical reactions involved in the process and influences the chemical and physical characteristics of the products generated (de Lima Veloso et al., 2022; Hossain et al. 2009; Siebeneichler et al., 2017). For most biomasses, the increase in temperature and reaction time reduces the final production of bio-oil and activated carbon, favoring the formation of gases. However, these associated factors favor an increase in the structural organization of the activated carbon produced. Prolonged heating and elevated temperatures can cause the cell walls to collapse, leading to an increase in the pore volume of the activated carbon obtained in the process. Paz et al. (2023) indicates that increasing the temperature of the pyrolysis process favors the production of activated carbon with higher iodine number values, and consequently better adsorption conditions for this material.

Temperature is the main factor in the thermochemical process of pyrolysis. The reactions that occur during this endothermic process are totally related to the effect of the temperature to which the biomass is subjected (Pedroza et al., 2014; Paz et al., 2023; Pedroza, Neves et al., 2021). Temperature is a main parameter that influences the yield of desired end products such as: solid fractions (coal), liquids and non-condensable gases. The higher the temperature, the higher the degree of thermal decomposition of the biomass, with a consequent increase in the liquid and gaseous fraction, consequently lower coal yield.

Figure 8 shows the values predicted by the statistical model from the experimental design versus values observed after the pyrolysis process.

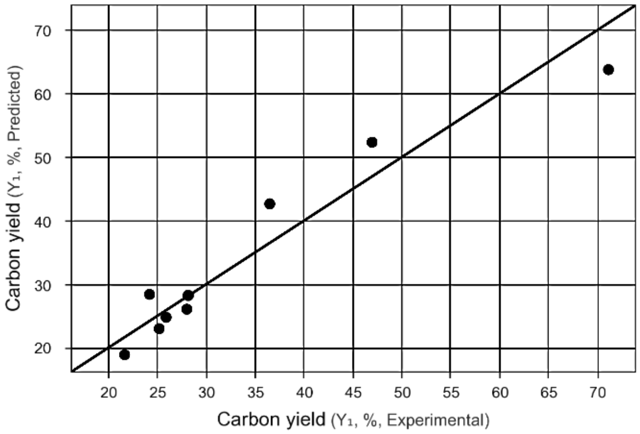

Figure 8. Observed versus predicted values for obtaining activated carbon yield.

It is also considered that the reactor used in the study of the thermal degradation of corn cob has a mechanism that hinders the exit of the vapors formed in the reaction, and this may have contributed to the condensation of liquids in the reactor extension. With a greater permanence of pyrolytic vapors inside the reactor, secondary reactions may occur that provide greater formation of coal in the system (Bridgwater, 2012; Pedroza, Neves et al., 2021).

Table 6 shows the effects of the variables studied in obtaining activated carbon during corn cob pyrolysis in a fixed bed reactor. The effects of interaction between the variables were disregarded. Significant effects are highlighted in bold (at a 95% confidence level). Temperature (p = 0.0015) and mean (p = 0.003) were the only significant effects on the solid fraction yield of the corn cob pyrolysis process.

With the regression coefficients, it was possible to write the adjusted model that describes the obtaining of activated carbon from the pyrolysis of corn cob biomass, according to Equation 2. The effects of mean (28.14) and temperature (-12.50) were significant at a 95% confidence level.

$$Yield\ (\%) = (28{,}14 - 12{,}5X_1 + 8{,}93\ {X_1}^2 + \ 0{,}63X_2 - 2{,}16{X_2}^2 - 4{,}1X_1.X_2) \qquad (2)$$

Where: X_1 = Temperature; X_2 = Heating rate.

Table 7 presents the analysis of variance (ANOVA) for activated carbon production in corn cob pyrolysis for an R^2 of 92.46% and Ftab (5; 5; 0.05) = 5.05.

R^2 coefficient obtained by the regression was 0.9246, indicating a good fit of the model, with an agglomeration of points close to the representative line.

The efficiency of the model by ANOVA analysis was performed using the F test, determined by the following formula (F calculated = mean square regression/mean square error), which was obtained for F calculated (12.3), and for the F tabulated regression (5.05). The value of F calculated must be greater than the value of F tabulated for a statistically significant model (Paz et al., 2023). Therefore, the experimental data obtained are well represented by the adjusted statistical model and can be used for predictive purposes in the region adopted by the factors (temperature and heating rate).

Response surface analysis shows a strong influence of temperature on activated carbon production during the process. The regions highlighted in red in Figure 9, indicate the conditions of greater production of activated carbon, from the pyrolysis of corn cob. This optimal area was experimentally determined with the following combinations between the variables studied here: (a) temperature (360 to 400 °C) and (b) heating rate (25 to 27 °C/min).

The statistical model obtained can be used to estimate the production of activated carbon only in the ranges used for the two factors used in the experimental design of this research: (a) temperature (360 - 640 °C) and (b) heating rate (13 - 27 °C/min).

The drying kinetics of the in natura biomass was performed at a temperature of 40 °C and it was observed that, in the first 9 hours, there is a loss of 75% of mass in the period. Assuming an activated carbon yield equal to 24.22% at a temperature of 640 °C, a production of approximately 61 kg of activated carbon is estimated for each ton of waste used in this research.

Table 6. Regression coefficients of the CCRD planning.

Name	Coefficient	Standard error	Calculated T	p-value
Mean	**28.14**	**3.23**	**8.72**	**0.003**
X_1	**-12.50**	**1.98**	**-6.33**	**0.0015**
X_1^2	8.93	2.35	3.80	0.0127
X_2	0.63	1.98	0.32	0.7625
X_2^2	-2.16	2.35	-0.92	0.3998
$X_1 . X_2$	-4.21	2.80	-1.51	0.1922

Table 7. ANOVA table for activated carbon production.

Variation source	Sum of squares	Degrees of freedom	Mean square	F_{calc}	p-value
Regressão	1917.3	5	383.5	12.3	0.00780
Resíduos	156.3	5	31.3		
Falta de Ajuste	156.3	3	52.1	25627.1	0.00004
Erro Puro	0.0	2	0.0		
Total	2073.7	10			

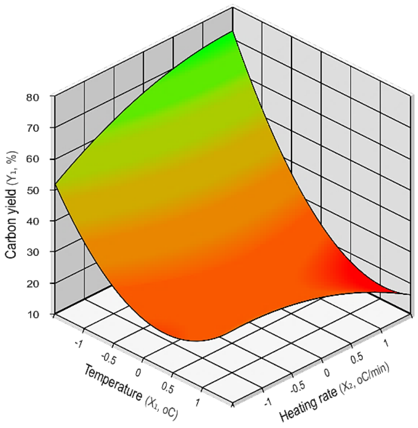

Figure 9. Response surface for activated carbon yield of corn cob pyrolysis.

3.3. Characterization of activated carbon

The activated carbon used in the analyses presented below was obtained under the following conditions: (a) 500 °C, (b) 20 °C/min and (c) 30 minutes. The results obtained through the analysis at the Larsen Laboratory are shown in Table 8, in addition to the relative contents of immediate analyzes of activated carbon samples cited in the literature. Where: SM: corn cob, PD: tree pruning; BC: sugarcane bagasse and FC: coconut fiber.

The ash content of the activated carbon produced was 17.09%. The ash present in activated carbons comes from oxides and compounds in smaller amounts such as phosphates, sulfates, chlorides, carbonates, and silicates. The amount of ash is dependent on the raw material used to obtain the charcoal and on the activation method, however its presence is undesirable because it alters the pH of solutions and contaminates them with salts (Bridgwater, 2012; Biswas et al., 2017).

The content of volatile materials was 38.68%. The increase in temperature in the carbonization treatment causes partial decomposition of organic matter and partial removal of volatiles, expelling them from the interior of the coal, which determines a lower content of volatiles and an increase in in the fixed carbon content at the end of the product as observed in the research (Chen et al., 2014; Pedroza et al., 2022).

The elemental analysis of the activated carbon obtained through the process of pyrolysis of the corn cob biomass is shown in Table 9.

In the research conducted by Mullen et al. (2010), it is observed that the percentage of carbon in the activated carbon obtained in the pyrolysis process was 71.64%, a value close to that found in the present work (72.34%). The values for the hydrogen content, in turn, are close to those obtained by Bavaresco et al. (2017), while for the nitrogen and oxygen contents, they are close to those presented by Mullen et al. (2010). No sulfur was identified in the constitution of activated carbon obtained in this research. The C/H ratio in activated carbon (90.4) was much higher than that obtained for biomass (C/H = 6.7).

The average volumetric density of the corn cob activated carbon obtained in the tests at the Larsen Laboratory was 0.103 g/mL. The pH of the activated carbon was obtained at room temperature, with a value of 7.8. This pH is close to neutral, despite being slightly alkaline. The study of pH is important in adsorption systems. Coals, in general, develop charges at the solid-liquid interface due to the dissociation or adsorption of ions from the solution (Marin et al., 2014). The characterization of these loads is important regarding the applications of materials as adsorbents, there is a pH range in which the net surface loads of the adsorbent are null (Zero Load Point of the adsorbent).

Table 8. Immediate analysis of different carbons.

Carbon	Moisture (%)	Volatile Material (%)	Ash (%)	Fixed Carbon (%)	Researchers
SM	3.43	38.68	17.09	40.80	This research
SM	-	39.83	4.00	56.17	Alves et al. (2016).
PD	2.80	23.06	9.60	67.34	Pedroza, Neves et al. (2021).
FC	4.85	29.90	13.03	58.07	Paz et al. (2023).

Table 9. Elemental analysis of corn cob carbon.

Elements					Researchers
C (%)	N (%)	H (%)	O (%)	S (%)	
72.34	**1.20**	**0.80**	**25.66**	-	This Research
71.64	1.23	3.40	23.73	-	Mullen et al. (2010).
84.87	1.83	1.15	11.78	0.04	Bavaresco et al. (2021).

3.4. Iodine number and adsorption tests

Activated carbon obtained at 640 °C showed an iodine adsorption capacity of 820 mgI_2/g, while the activated carbon produced at 600 °C had an iodine number of 701 mgI_2/g.

Onu et al. (2022) and Iheanacho et al. (2021) obtained activated carbon from corn cob with an iodine number of 888.34 mg/g and 888.35 mg/g, respectively. Song et al. (2013) compared the number of iodine between thermophysical activated (steam) and thermochemically activated (KOH) corn cob charcoal, obtaining 665.23 mg/g and 1262.25 mg/g, respectively.

Table 10 presents the Thomas model coefficients obtained during the methylene blue adsorption tests in a filtration column using activated carbon obtained from the thermal degradation of corn cob. Activated carbon used here was produced under the following conditions: (a) temperature = 500 °C, (b) heating rate = 20 °C/min and (c) pyrolysis time = 30 min.

Table 10. Thomas model coefficients.

Model parameters	Flow (mL/min)	
	5.1	9.9
K_{TH} (mL/mg.min)	0.0046	0.0093
q_o (mg/g)	54	98
R^2	0.95	0.97

With the slope and intercept of the graph of ln(Co/Cx – 1) versus t, the rate constant (K_{TH}) and the maximum adsorption capacity (q_o) were determined, with a strong negative relationship between ln(Co/Cx – 1) and “t”. The Thomas model is employed in a fixed bed adsorption system with continuous flow. The adsorption process follows the Langmuir isotherm, not considering the effects of radial and/or axial dispersion, and admits reversible second-order kinetics (Thomas, 1944).

The methylene blue dye adsorption system remained in operation for 24 hours, with the average flow and concentration of the filtered effluent being measured every 30 minutes.

The filter showed maximum removal in the first 1 liter of the dye solution under study, operating at an average flow rate of 5.1 mL/min. A decrease in removal efficiency is also observed due to activated carbon saturation. The lowest efficiency observed was 63 % with an operating time of 630 minutes.

The values obtained by fitting the experimental data to the Thomas model were K_{TH} = 0.0093 mL/mg.min and q_o = 98 mg/g, when a liquid flow equal to 9.9 mL/min was used.

It is possible to notice that with the increase in the flow rate from 5.1 to 9.9 mL/min, there is an increase in the adsorption capacity, qo , of the column. The mass transfer coefficient, K_{TH}, also increases with increasing flow rate. The increase in the transfer coefficient occurs because when the feed flow rate increases, the resistance at the liquid film interface decreases, increasing the mass transfer coefficient (Zhang et al., 2011). The decrease in resistance at the film interface is due to the decrease in the boundary layer, which allows greater mass transfer in the adsorbent material. Bernal et al. (2021) state that the increase in liquid flow can cause turbulence in the column, which can generate variations in the mass transfer zone.

Han et al. (2009) studied adsorption in a fixed bed column using phoenix tree leaf powder as an adsorbent for the removal of methylene blue from aqueous solution. According to research observations, with the increase in flow, K_{TH} value increased. Values of the constant qo (m/g) of 125 and 132 were determined when the column was operated with dye solution flow rates (mL/min) equal to 8 and 12, respectively.

The coefficient R^2 presents a higher value for a flow rate of 9.9 mL/min, showing a better fit of the experimental data to the model in relation to a flow rate of 5.1 mL/min. The values of the R^2 correlation coefficients obtained for the Thomas model were greater than 0.95, which indicates that the model adopted in this research had a good prediction of dye adsorption with activated carbon, for the highest liquid flow rate.

The use of corn on the cob to produce activated carbon provides greater income generation for farmers, as it adds greater value to these by-products, giving them new forms of reuse. On the other hand, activated carbon producers, regardless of the production scale to which they are dedicated, have felt the impacts on operating costs due to the growing demands of using labor and acquiring raw materials in a legal way, meeting, at the same time, to calls for cleaner production with low levels of pollution. The search for alternatives that meet all these purposes in an economical way leads to the need for more efficient processes.

According to Torre et al. (2008) and Tsai et al. (2001), approximately 180 kg of corn cob are generated for each ton of processed corn. Assuming a production estimate of 665 thousand tons of corn processed in Tocantins in the 2017 harvest (Paz et al., 2023) and observing the approximate average yield of activated carbon production of 33% from pyrolysis in a bed reactor fixed, activated carbon production of up to 39,500 tons can be obtained from corn cob.

4. Conclusions

The carbon content (44%) and the lignin content (28%) point to the use of residual biomass studied in this research to produce activated carbon by thermal route. Temperature had a negative effect (-12.50) on activated carbon production. Activated charcoal yields ranged from 21.6% (600°C) to 71.12% (360°C). It is observed that elevated temperatures promote greater thermal degradation of the biomass causing a reduction in the carbon content in the fixed bed reactor studied in this research. The heating rate had no significant effect on the production of activated carbon, indicating that the fixed bed reactor studied can operate at the highest level adopted for this variable in the range studied here, thus providing a shorter heating time of the system and consequently a shorter energy expenditure. The temperature used during biomass pyrolysis interferes with the quality of the activated carbon obtained. A higher reactor temperature favors obtaining the adsorbent material studied here with a higher iodine number. The adsorbent material produced in this research presented the following iodine number values: 820 mgI2/g (640 oC) and 701 mgI2/g (600 oC). Thomas model coefficients were obtained: kTH = 0.0093 mL/mg.min and qo = 98 mg/g, when a liquid flow rate equal to 9.9 mL/min was used in the adsorption tests. The adsorption capacity of the material is related to the flow rate of the dye solution used in the tests. Higher liquid flow rate favors a higher adsorbate mass transfer coefficient.

Conflict of interest

The authors do not have any type of conflict of interest to declare.

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