

Effect of calcination temperature on material from an ant colony (termite): searching for the characterization of new dye adsorbent materials

Efeito da temperatura de calcinação em material proveniente de uma colônia (cupim): buscando pela caracterização de novos materiais adsorventes

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ABSTRACT

The reuse of contaminated water arising from industries is a major challenge in the environmental field, which enables the search for treatments with a view to sustainable development. In this context, the objective of this study was to evaluate the effect of the calcination material from an ant colony (termite) in the production of adsorbent materials for methylene blue dye removal. The natural material (NC) and calcined materials at temperatures of 290°C (C-290), 380°C (C-380), 450°C (C-450) and 540°C (C-540) were characterized using techniques of thermal analysis and Fourier Transform Infrared Spectroscopy (FTIR). In NC and C-290 samples, the volatile compounds were evaluated by HS-GC/MS and phenolic compounds were identified by HPLC. The results for the adsorption of the dye methylene blue showed that, while the adsorption process can not be quantified employing the natural material, the process efficiency was quite relevant when the sample was calcined at a temperature of 290°C, whose removal percentage was 96%. Although the calcined sample at this temperature is the most similar to the starting material, performed at a temperature of 290°C acted in reducing the complexity of phenolic and volatile compounds found in the NC sample, which may negatively impact in the adsorption process.

Keywords: adsorption, volatile compounds, phenolic compounds.

RESUMO

O reaproveitamento da água contaminada decorrente das indústrias é um grande desafio na área ambiental, o que possibilita a busca de tratamentos com vistas ao desenvolvimento sustentável. Nesse contexto, o objetivo deste estudo foi avaliar o efeito do material de calcinação de uma colônia de formigas (cupim) na produção de materiais adsorventes para remoção do corante azul de metileno. O material natural (NC) e os materiais calcinados a temperaturas de 290°C (C-290), 380°C (C-380), 450°C (C-450) e 540°C (C-540) foram caracterizados por meio de técnicas de análise térmica e Espectroscopia de Infravermelho com Transformada de Fourier (FTIR). Nas amostras NC e C-290, os compostos voláteis foram avaliados pelo HS-GC/MS e os compostos fenólicos foram identificados pelo HPLC. Os resultados para a adsor-

ção do corante azul de metileno mostraram que, embora o processo de adsorção não possa ser quantificado utilizando o material natural, a eficiência do processo foi bastante relevante quando a amostra foi calcinada a uma temperatura de 290°C, cujo percentual de remoção foi de 96%. Embora a amostra calcinada a esta temperatura seja a mais semelhante ao material inicial, a calcinação na temperatura de 290°C atuou na redução da complexidade dos compostos fenólicos e voláteis encontrados na amostra de NC, os quais podem prejudicar no processo de adsorção.

Palavras-chave: adsorção, compostos voláteis, compostos fenólicos

1. INTRODUCTION

In recent decades, environmental issues have become increasingly critical and frequent, mainly due to population growth and increased industrial activity. The scarcity of water resources, coupled with the pollution of natural waters, is considered one of the major problems of modern society. Therefore, the economy and reuse of water in production processes are highlighted due to its value [1].

Industries in which dyes are employed are responsible for the contamination of natural waters. Their activities produce large amounts of waste containing reactive dyes, which, although not toxic, can undergo partial biological degradation. This contamination can also result from other treatment forms that cause the partially degraded molecules to bind to other molecules, leading to the formation of much more toxic compounds than the original dyes [2].

Industries produce effluents that have strong coloration, large amounts of suspended solids, highly fluctuating pH, high temperature and high concentrations of chemical oxygen demand (COD) [3]. In addition to visual pollution, these compounds cause changes in biological cycles, mainly affecting the photosynthesis process. Furthermore, studies have shown that some classes of dyes can be carcinogenic and/or mutagenic [4].

Adsorption is one of the processes used for removing these dyes. It is characterized as a mass transfer process, which exploits the ability of certain solids to concentrate specific substances contained in aqueous solutions or in gases on their surface, resulting in a separation involving interactions between system components [5].

In general, satisfactory results in the removal of effluents are based on traits associated with the choice of materials that have high adsorption capacity, to reduce the amount of adsorbent used; high internal and external surface area, capable of increasing adsorption capacity; high selectivity, necessary to perform an appropriate separation; thermal and chemical stability; low solubility, to preserve the traits of adsorption and adsorbent; hardness and mechanical strength, which avoid pore constriction and particle erosion, in addition to not allowing undesirable chemical reactions [6, 7].

Although activated carbon is described as the most suitable adsorbent for removing contaminants, studies have reported a reduction in its applicability, given that it presents disadvantages such as high production costs and difficult regeneration, considered key factors of the economic viability of the process [7].

In this context, this research was developed in order to use solid materials that, in addition to being able to remove pollutants from contaminated water, present low-cost and regenerate, parameters considered ideal for sustainable development [7].

These low-cost materials require little processing or are abundant in nature. They include industry by-products or waste materials, such as macaúba meal [8] and castor bean meal [9], waste from biodiesel production and agricultural solid waste, such as orange and uvaia seeds [10], soybean hull [11], cotton waste [12], coconut shell [13], sugarcane bagasse [14], sisal fiber [15], orange peel [15]. They also include natural materials represented by montmorillonite clay [16], bentonite [17], diatomite [18], perlite [19] and pyrophyllite [20].

Leaf-cutting ants belonging to the Attini tribe developed a mutualistic interaction with some fungal species. Plant material collected by worker ants (leaves, seeds, fruits) serves as a substrate for the fungi, which, in turn, is food source for the ants. However, mutualism between ants and fungi exists thanks to sophisticated disease containment mechanisms among the members of the colony, which also prevent the ant colony from being contaminated with pathogens and saprophytes. First, ants in charge of forage clean the collected plant material, removing contaminating material from the surface. Leaf-cutting ants also perform self-cleaning and mutual cleaning. As a chemical protection, the ants present metapleural glands that secrete antiseptic compounds, and it is possible to observe symbiosis with antibiotic-secreting bacteria that live associated with their teguments [21].

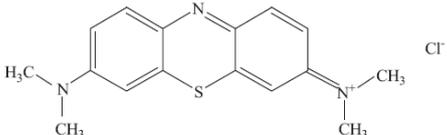
Given the aforementioned, the objective of this study was to evaluate the effect of calcination over material obtained from an ant colony for the production of adsorbent materials using methylene blue as model molecule.

2. MATERIALS AND METHODS

Adsorbate

The methylene blue solution used in the adsorption studies was prepared from a stock solution at a concentration of 1000 mg L⁻¹. The chemical structure, as well as the properties and traits of methylene blue, are described in Table 1.

Table 1: Properties and characteristics of methylene blue dye

Generic name	Methylene blue
Chemical name (IUPAC)	3,7-bis(dimethylamino)-phenothiazin-5-ium chloride
Number CAS	61-73-4
C.I.	52015
Chemical formula	C ₁₆ H ₁₈ CIN ₃ S
Molecular weight (g mol ⁻¹)	319.85
Chemical structure	

Adsorbents

The natural material (NC) was obtained from an ant colony located in an altitude field, near the town of Itumirim, southern Minas Gerais, Brazil. The natural sample was subjected to heat treatment, conducted in a muffle furnace (FORNOS MAGNUS- Model 200 F) for 3 hours, at a heating rate of 10°C min⁻¹, and at temperatures of 290°C (C-290), 380°C (C-380), 450°C (C-450) and 540°C (C-540).

2.1 Adsorbent Characterization

In order to verify the thermal stability of the natural material (NC) and calcined samples, we conducted a thermogravimetric analysis on a thermomechanical analyzer (Shimadzu DTG-60H). Approximately 5.0 mg samples were used, heated at a rate of 10°C min⁻¹, from 25°C to 800°C, under synthetic air flow.

The functional groups were analyzed by Fourier transform infrared vibrational spectroscopy (FTIR), using the IR Affinity equipment, with a spectral range of 4000-400 cm⁻¹, 64 scans and 4 cm⁻¹ resolution.

Volatile organic compounds (VOCs) were extracted by headspace at 80°C for 10 minutes, using 1.0 g of the materials NC and C-290, in addition to 100 µL steam for injection. Gas chromatograph coupled to a mass spectrometer - GC-MS QP2010 Plus (Shimadzu, Japan), equipped with an AOC-5000 automatic injector for liquids and gases (Shimadzu, Japan) and a 30 m × 0.25 mm × 0.25 µm SLBTM column (5% phenyl-95% dimethylsiloxane), were used to separate and identify volatile organic compounds. The injector temperature was kept at 260°C, operating in splitless mode. Helium was used as carrier gas, at a flow rate of 1.00 mL min⁻¹. The temperature of the oven was programmed at 40°C, remaining for 2 minutes, and placed on heating ramp from 6°C min⁻¹ to 300°C, remaining for 2 minutes. An electron impact (70 eV) mass spectrometer was used in scan mode (30 to 300 Da), with solvent cut time of 2.00 min. The temperature of the detector interface and of the ion source remained at 250°C and 200°C, respectively. The volatile compounds were identified comparing the mass spectra obtained with the mass spectra found in literature [22].

To determine the phenolic compounds released into the water, 0.10 g of the NC materials and C-290 were placed in contact with 10 mL aliquots of deionized water and stirred at 100 rpm for 24 hours. Supernatant aliquots of 8 mL were collected and lyophilized. The samples were then resuspended in 5 mL of HPLC grade methanol and filtered at 45 µm. The identification and quantification of the phenolic compounds was performed using Shimadzu high performance liquid chromatography analysis equipped with a quaternary pump (LC-20AT), diode array detector – DAD (SPDM-20A), degasser (DGU-20A5), model interface (CBM-20A) and an automatic injector with autosampler (SIL-20A). Separations were made using a Shim-pack VP-ODS C18 column, of 25 cm x 4.6 mm (internal diameter) x 5 µm and a Shim-pack GVP-ODS C18 pre-column, of 10 mm x 4.6 mm (internal diameter) x 5 µm.

We performed elution in a gradient-type system: 0 to 5 min (0-30% B); 5 to 25 min (30-40% B); 25-43 min (40-45% B); 43 to 50 min (45-80% B); 50 to 55 min (80-0% B); 55 to 65 min (0% B). The mobile phases consisted of water:acetic acid (98:2% v/v) (Mobile Phase A) and water:acetic acid:acetonitrile (70: 28: 2% v/v) (Mobile Phase B). The flow rate used throughout the analysis was of 1.00 mL min⁻¹, with injected volume of 20 µL, for samples and standard, analyzed at 280 nm.

Compound identification in samples NC and C-290 was conducted by comparing sample retention time to that of the standards. Quantitation was performed using external standardization. All samples were analyzed in duplicate, while working solution standards were analyzed in triplicate. The detection (DL) and quantitation (QL) limits of the method were calculated based on the parameters for each constructed analytical curve, using the following mathematical relations [23, 24]:

$$DL = 3x \left(\frac{s}{S} \right)$$

(1)

$$QL = 10x \left(\frac{s}{S} \right)$$

(2)

in which s is the estimated standard deviation of the response, which can also be the estimated standard deviation of the blank, regression line equation or linear line equation, and S is the slope or the angular coefficient of the calibration curve.

Adsorption experiments

Experiments were conducted in batch and in triplicate, in order to verify the effect of calcination over the efficiency of the material in adsorbing methylene blue (MB) dye.

For the adsorption tests, 10 mL aliquots of the dye solution, at a concentration of 25 mg L^{-1} and natural pH ($\text{pH} = 6.5$), were placed in contact with 0.10 g of the materials sieved at 50 Mesh. The systems were stirred at 100 rpm on a shaker table (II CERTOMAT MO) at room temperature ($25 \pm 1^\circ\text{C}$).

After a stirring time of 24 hours, the supernatants were separated and the remaining dye concentrations were determined at a wavelength of 665nm using a Shimadzu UV-1600 spectrophotometer. The removed percentage was then calculated using the following equation [3]:

$$\% R = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

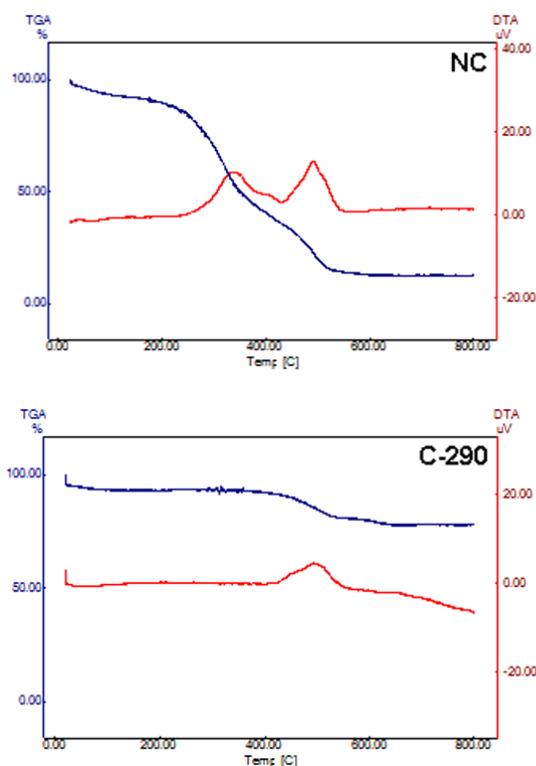
in which C_0 is the initial concentration of the dye and C_t , the concentration of the dye at time t .

The unsupervised pattern recognition analysis was applied to the data in order to verify the correlation between the samples, as well as to evaluate the similarity. For this purpose, Principal Component Analysis (PCA) and Hierarchical Component Analysis (HCA) were applied. The samples went through the auto-scaling pre-processing, using Euclidean distance, where the data were connected by the nearest neighbor. Chemoface software version 1.5 was used for the chemometric analysis [25].

3. RESULTS AND DISCUSSION

3.1 Adsorbent Characterization

The Figure 1 shows the thermal analysis of the natural material (NC) and calcined materials at temperatures of 290°C (C-290), 380°C (C-380), 450°C (C-450) and 540°C (C-540).



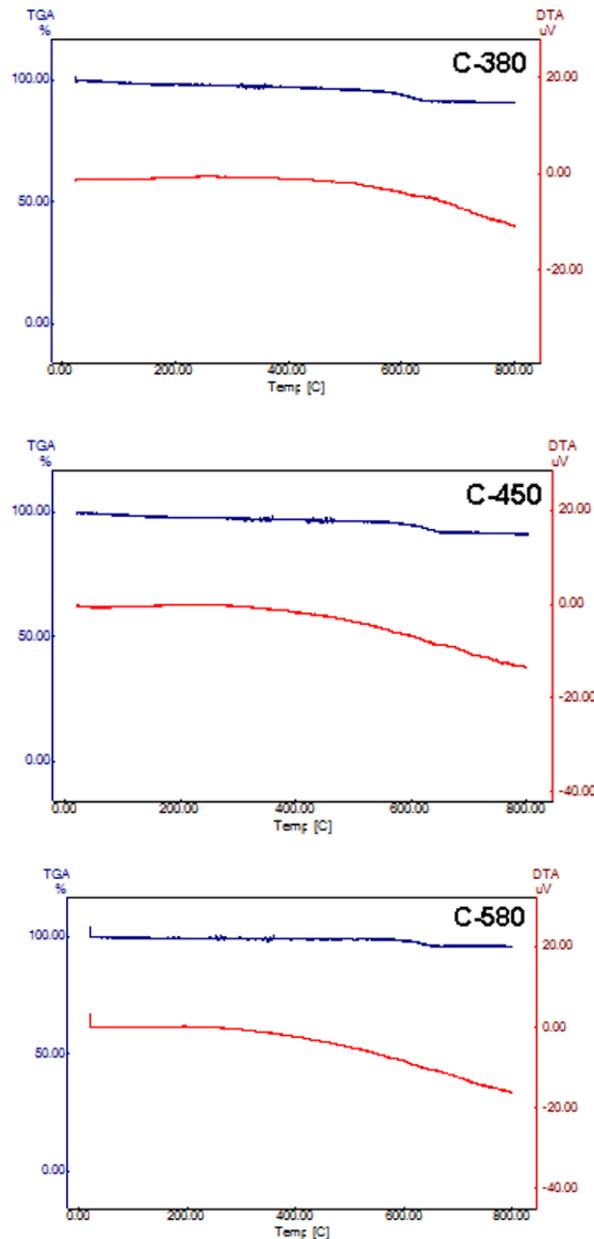


Figure 1: Thermal analysis of samples: natural (NC) and calcined (C-290, C-380, C-450, C-540)

The Figure 1 shows that the NC sample has two mass loss regions. While the first (52%), close to 300°C, is attributed to thermal degradation of cellulose and hemicellulose [25], the second (22%), in the region above 400°C, is associated with the degradation of lignin, considered more stable than cellulose and hemicellulose polymers [8]. Such losses are associated with the presence of undergrowth vegetation surrounding the location from which the starting material was collected.

It is possible to observe that calcination at a temperature of 290°C (C-290) led to the degradation of cellulose and hemicellulose. Treatments conducted at other temperatures degraded the starting material, making it thermally stable, given the lack of significant mass losses [26].

FTIR spectra of the materials and the identification of characteristic bands are shown in Figure 2 and Table 2, respectively.

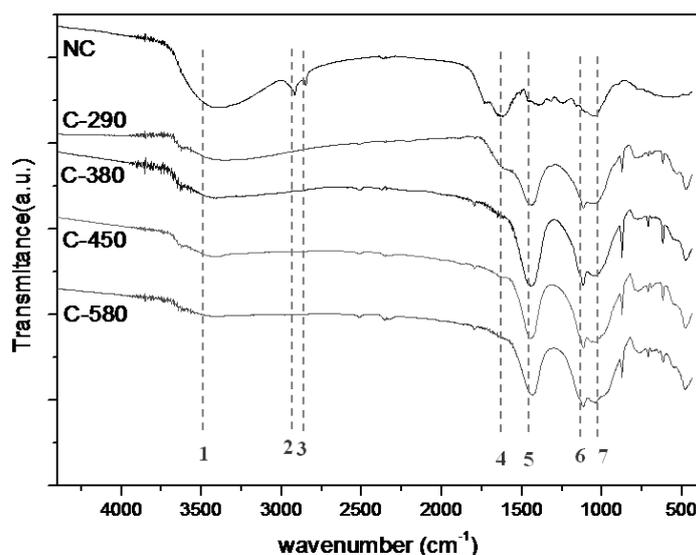


Figure 2: Spectra obtained through the analysis of samples by FTIR

Table 2: Assignment of IR absorption bands

Signal	Wavenumber (cm ⁻¹)	Assignment	Characterization	References
1	3404	Free and intermolecular bonded hydroxyl groups	Cellulose	[27–29]
2	2916	Antisymmetric C-H ₂	Fat.wax and lipids	[27, 29]
3	2845	Symmetric C-H ₂	Fat.wax and lipids	[27, 29]
4	1635	C=C stretching and/or asymmetric C-O in COO-	Lignin or other aromatics groups and/or aromatic or aliphatic carboxylates	[27, 29]
5	1457	C-H deformation	Aliphatic structures	[27, 29]
6	1125	combination of C-O stretching and O-H deformation	Combination of C-O stretching and O-H deformation	[27, 28]
7	1035	combination of C-O stretching and O-H deformation	Combination of C-O stretching and O-H deformation	[27, 28]

For calcined samples, we verified the disappearance of bands located at 3404 cm⁻¹, 2916 cm⁻¹ and 2845 cm⁻¹, which allows us to infer that treatments conducted at all studied temperatures were responsible for the cellulose degradation. These results are consistent with those obtained by thermal analysis. The reduction in intensity for the band located near 1635 cm⁻¹ in the C-290 sample, as well as its disappearance in samples C-380, C-450 and C-540, showed that, at a milder calcination temperature (290 °C), no complete degradation of lignin was observed, given that this compound is more stable than cellulose and hemicellulose [26].

3.2 Comparative analysis of samples using pattern recognition

Principal Component Analysis (PCA) and Hierarchical Component Analysis (HCA) consist of exploratory or unsupervised methods applied in treatments of which data results involve a large number of variables, according to data obtained from the analysis in the infrared region. These methods provide graphical representation of the entire dataset, facilitating result interpretation when sample similarity verification is desired.

In this context, in order to verify the effect of calcination temperature over the NC sample, we analyzed sample similarity by comparative analyses of the intensities of the bands observed in the infrared region, within spectral range between 4000 cm⁻¹ and 400 cm⁻¹. The results of the PCA analysis are presented in Figure 3a.

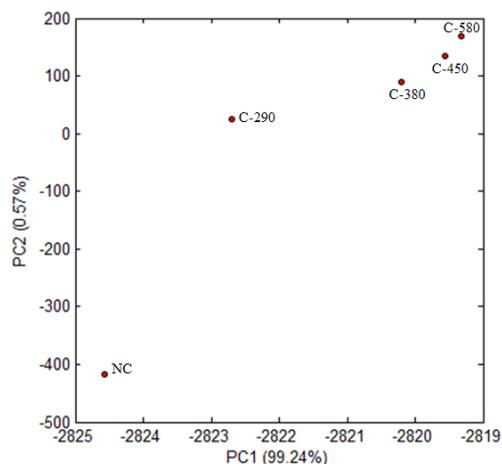


Figure 3a: Scores plot obtained from FTIR analysis

Taking into account the first two main components, which retain 99.81% of the dataset information, the results described by the PCA analysis show the existence of two distinct groups. One comprising samples C-290, C-380, C-450 and C-540, and another formed by sample NC. The results obtained by principal component analysis are confirmed by dendrogram obtained by means of HCA. The HCA shows the similarity index of the samples. The results are presented in Figure 3b.

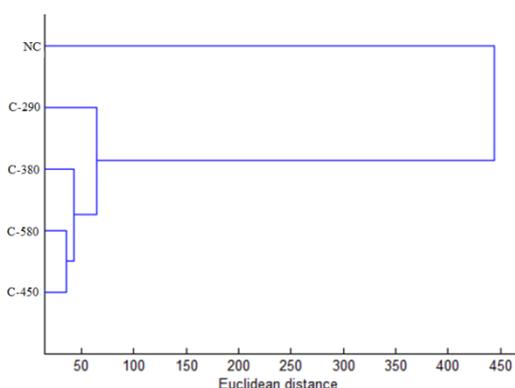


Figure 3b: Dendrogram obtained from FTIR analysis

Considering the Euclidean distance and the type of bond with the nearest neighbor, the results in Figure 3b show that samples C-450 and C-540, calcined at 450°C and 540°C, respectively, presented higher similarity, given the smaller Euclidean distance observed between them. The group formed by these samples was similar to sample C-380, calcined at 380°C, forming, in turn, another group with sample C-290, of which heat treatment was conducted at 290°C. We also observed that, among the calcined samples, sample C-290 showed higher similarity with sample NC. These results allow us to infer that the lowest calcination temperature caused a minor variation over the starting material, since it is conducted at a milder temperature, presenting smaller reducing effect over the characteristic bands of the NC sample, among which, that associated with lignin, located at 1635 cm^{-1} , is highlighted.

3.3 Methylene blue adsorption study

In order to verify the possibility of using materials as adsorbents of methylene blue dye, as well as to evaluate the influence of possible interfering substances over the adsorption process, natural (NC) and calcined (C-290, C-380, C-450 and C-540) samples were pre-stirred with water for 24 hours. The results are showed in Figure 4.



Figure 4: Results obtained from the agitation of the samples with water (IN- *in nature* or natural material (NC) and calcined materials (A, B, C and D)

We noted that the sample NC (IN) released compounds with a strong yellow coloration after 24 hours of stirring, as can be seen in Figure 4.

These compounds present in the starting sample are possibly of phenolic origin, which prevented the adsorption quantification of this sample. The results that were conducted only with calcined samples are presented in Figure 5.

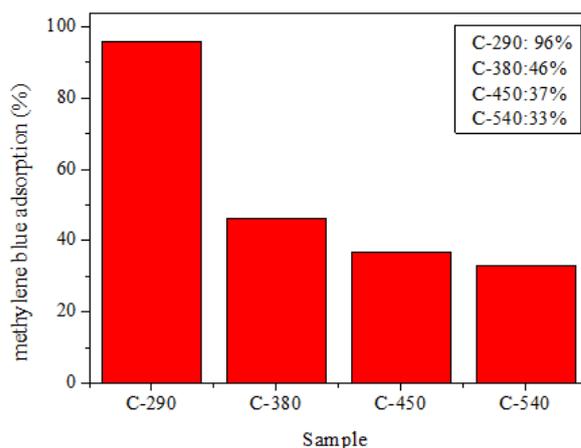


Figure 5: Results of methylene blue adsorption in the calcined samples

It is possible to observe a decrease in dye adsorption as the calcination temperature increased. These results may be associated with the increased degradation of the starting material constituents, which present the functional groups responsible for the adsorption mechanism [26]. The observed data also showed that the calcination temperature of 290°C stood out for producing a material suitable to be applied as an adsorbent of methylene blue dye. The results obtained are in agreement with the FTIR analysis (Figure 2).

Based on these results, a comparative analysis of volatile and phenolic compounds was conducted with samples NC and C-290, given that this material, calcined at 290°C, produced the adsorbent material most efficient in removing methylene blue dye.

The Figure 6 shows the HPLC analyses that were conducted in order to identify the presence of phenolic compounds in water and in sample C-290 after contact for 24 hours.

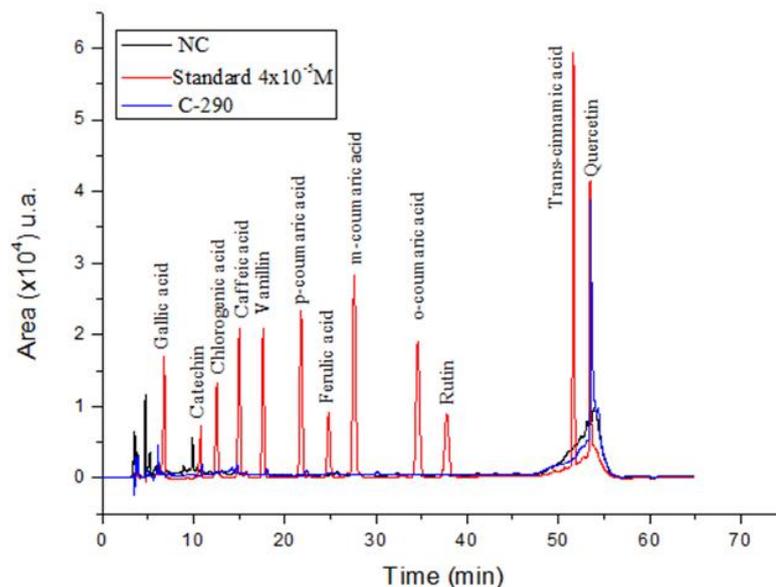


Figure 6: Chromatogram of the phenolic compounds in the samples (NC and C-290) and standard

The presence of phenolic compounds is observed in samples NC and C-290 (Figure 5). The former showed a higher phenolic complexity. The high complexity of phenolic compounds found in the NC sample is associated with the fact that this complex group of constituents is part of a wide variety of vegetables, among which the undergrowth vegetation near the altitude field from which the sample was collected stands out in this study [30, 31].

The analytical curves of phenolic compounds, as well as the detection limits and pattern quantification used, are presented in Table 3.

Table 3: Phenolic compounds that were identified in the samples: NC and C-290

Compound	Equation ($y = a + bx$)	Correlation coefficient (r^2)	DL ($mg L^{-1}$)	QL ($mg L^{-1}$)	Concentration ($mg L^{-1}$)	
					NC	C-290
Gallic acid	$739.34+39462.43x$	0.9965	0.17	0.58	ND	ND
Catechin	$-233.23+11791.68x$	0.9964	0.30	0.99	<LQ	ND
Chlorogenic acid	$-1385.52+18390.60x$	0.9970	0.14	0.47	<LD	<LQ
Caffeic acid	$944.17+62088.92x$	0.9932	0.30	1.01	ND	ND
Vanillin	$-23.52+76751.89x$	0.9988	0.09	0.30	ND	<LQ
p-coumaric acid	$-2298.79+91753.99x$	0.9926	0.24	0.81	<LD	ND
Ferulic acid	$-1414.19+33344.56x$	0.9957	0.10	0.34	ND	ND
m-coumaric acid	$-243.76+125590.67x$	0.9965	0.17	0.55	ND	ND
o-coumaric acid	$-1691.78+103445.77x$	0.9921	0.25	0.84	ND	ND
Rutine	$729.72+15343.50x$	0.9951	0.73	2.43	ND	ND
trans-cinnamic acid	$7304.50+169796.79x$	0.9972	0.13	0.45	ND	ND
Quercetin	$-3926.08+40590.76x$	0.9960	0.37	1.23	<LQ	<LD

DL = detection limit/ QL = quantification limit e ND=not detected

From the data presented in Table 3, we can infer that, from 12 phenolic compounds evaluated by this method, only four were detected in the NC sample and three in the C-290 sample. However, it was not possible to quantify them, given that they were all below the quantification limit of the method. With the results obtained, it is possible to detect compounds from the class of flavonoids (quercetin and catechin), responsible for the color observed in leaves, flowers and other plant parts. It was also possible to detect the phenolic compound hydroxyl cinnamic acid (p-coumaric acid) and a polyphenol (chlorogenic acid). The data presented in Fig. 5 shows that other phenolic compounds could be present in the NC material. However, they were

not evaluated in this study. The presence of such compounds can negatively influence the adsorption of methylene blue, since they are responsible for the intense coloration, which influences absorption in the UV-visible region, besides competing for adsorption sites in the NC sample.

In addition to the presence of phenolic compounds, the NC material also presents the complexity related to volatile composition. The compounds identified by HS/GC-MS are presented in Figure 7.

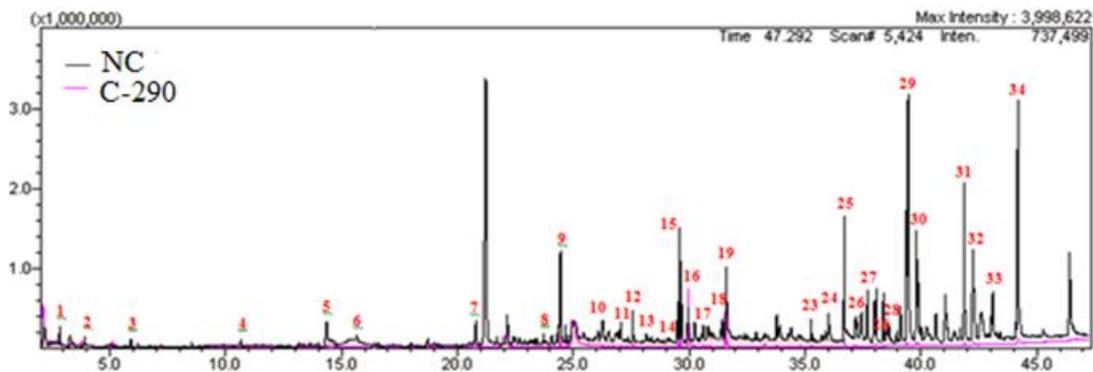


Figure 7: Chromatographic profile of volatile compounds identified by GC /MS in the samples (NC and C-290)

The peaks shown in the chromatogram are shown in Table 4.

Table 4: Identified peaks at Chromatographic profile of volatile compounds

Peak	Compound
1	acetic acid
2	butanal
3	hexanal
4	β -pinene
5	hexanoic acid, 2-ethyl
6	octanoic acid
7	methylcinnamate
8	δ - cadinene
9	trans-nerolidol
10	dibuthylphthalate
11	2-tetradecanone
12	hexa-hidro-farnesol
13	tetradecanoic acid
14	phytol
15	hexahydrofarnesylacetone
16	diisobuthylphtalate
17	3-eicosyne
18	isophytol
19	n-hexadecanoicacid
20	ethyl-hexyl-p-methoxycinnamate
21	dipentylphthalate
22	heneicosane
23	docosane
24	9-octadecenoic acid (E)

25	hexacosane
26	heptacosane
27	1-heptatriacotanol
28	pentadecane, 8-heptyl
29	monoethylhexylphthalate
30	heptadecane, 2,3-dimethyl
31	nonacosane
32	eicosane 2-methyl
33	squalene
34	hentriacontane

As occurs with phenolic compounds, these compounds might compete for sites of the adsorbent or release compounds in solution that influence the adsorption of methylene blue [32]. We can also observe in Fig. 6 that the calcination conducted at a temperature of 290°C reduced the amount of released volatile compounds, therefore producing a material suitable to be used as a dye of the studied adsorbent.

4. CONCLUSIONS

The results of the thermal analysis show that calcination temperatures of 380 °C, 450 °C and 540 °C were responsible for the production of stable materials. FTIR analyses showed that the increase in temperature led to a decrease in the characteristic band of lignin constituting the starting material. It was possible to verify that sample C-290 is highlighted, given the minor effect over this process, presenting greater similarity to the NC sample. The results from the methylene blue adsorption showed that the process was effective when using the calcination temperature of 290 °C because this temperature reduced the complexity of volatile and phenolic compounds.

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