

# Hierarchical Carbons from Banana Production Waste: A Sustainable Solution for n-Hexane Removal

José Luiz Cunha Cordeiro<sup>a,b</sup>, Rodrigo Santos Gonzaga Menezes<sup>a</sup>, Matheus Chaves Moreira da Silva<sup>a</sup>, Artur José Santos Mascarenhas<sup>a</sup>, Raildo Alves Fiuza-Júnior<sup>a,b</sup>

<sup>a</sup> *Laboratório de Catálise e Materiais (LABCAT), Instituto de Química, Departamento de Química Geral e Inorgânica, Universidade Federal da Bahia, Trav. Barão de Jeremoabo, 147, Campus de Ondina, 40170-280, Salvador, Bahia, Brazil. Site:*

*www.labcat.ufba.br; Instagram: @labcat.ufba*

<sup>b</sup> *Programa de Pós-Graduação em Energia e Ambiente (PGENAM), Centro Interdisciplinar de Energia e Ambiente (CIENAM), Universidade Federal da Bahia, R. Barão de Jeremoabo, s/n, Campus de Ondina, 40170-115, Salvador, Bahia, Brazil.*

## Abstract

Activated carbons were prepared from residues from agro-industrial banana production (banana pseudostem) and evaluated in the n-hexane capture. The biomass was first submitted to a hydrothermal treatment in the presence of K or Zn as activating agents, followed by a dry pyrolysis. VOC capture studies were performed by thermal analysis, and capture capacities were similar to or higher than those presented in the literature. Higher adsorption capacities were related to the amount of available micropores, and the capture capacity was enhanced by the contribution of small mesopores. As the highest adsorbed amounts of n-hexane (650 mg g<sup>-1</sup> at 25°C) were obtained for the material activated with Zn (1:3). Increasing n-hexane concentration on BZ13 carbon increased adsorption capacity (394-650 mg g<sup>-1</sup>). Adsorption capacity decreases with temperature rise in the adsorption isotherm (426-322 mg g<sup>-1</sup>), indicating physisorption governed by an exothermic process. The results indicate that the carbons produced here can be applied in n-hexane removal.

**Keywords:** activated carbon; n-hexane; adsorption

## 1. Introduction

Air pollution and its impacts on the environment and human health are current concerns, and scientific and technological development is needed to try [1]. Among the most commonly used Volatile Organic Compound (VOC) is n-hexane. Exposure to n-hexane vapors can cause significant health problems [2].

Porous activated carbons, especially those derived from biomass, are being widely used as adsorbents for capturing different VOCs [2]. Several methods can be applied to the production of activated carbons, and the hydrothermal route has been widely investigated, as it increases the capacity of biomass utilization, improving both the reactivity of precursors and surface chemistry of the carbon produced [3].

The adsorption capacity of n-hexane varies widely in the literature, but high adsorption values are usually not found. For example, values of 100 mg g<sup>-1</sup> are found in the literature [4]. Thus, the present work aims to advance the development of new hierarchical carbons derived from banana

pseudostems that can be applied to capture n-hexane.

## 2. Materials and Methods

### 2.1 Preparation and characterization of new hierarchical carbons

The banana pseudostems were collected on the campus of the Federal University of Bahia (UFBA), located in the city of Salvador, Bahia, Brazil. After collection, the material was cut into small pieces of approximately 2 cm x 2 cm and dried in an air circulation oven in three stages: (i) 60°C (24 h); (ii) 80°C (24 h); and (iii) 105°C (24h), applying at the end of the process the technical standards of preparation ASTM E1757 and E1756. Soon after, the biomass was crushed in a knife mill (Tecnal - ET-680) and sieved between 35 and 115 mesh (0.500 and 0.125mm).

The biomass was carbonized in the first step by hydrothermal treatment for 2 hours at 200°C, using a stainless-steel autoclave, with an inner PTFE cup, where 5 g of biomass and 80 mL of aqueous solution

of the activating agent was added. The activating solution was prepared using a biomass/activating agent ratio (1:1 or 1:3) using potassium hydroxide or zinc chloride. Soon after, the material was dried in an oven at 150°C until constant mass and heat treatment for 2 h, at 750°C, under a nitrogen flow of 150 mL min<sup>-1</sup> and a heating ratio of 5°C min<sup>-1</sup>. The obtained carbons were washed with a solution of 0.5 mol L<sup>-1</sup> hydrochloric acid to remove the carbonates and residues of the activating agent, followed by a new wash with deionized water. As a reference for the activation studies, a material without any chemical activation was produced using the same methods and named REF. The materials produced by activation of KOH were called BK11 and BK13 for the proportions 1:1 and 1:3, respectively, and the materials produced with ZnCl<sub>2</sub> were called BZ11 and BZ13 also for the proportions 1:1 and 1:3.

The textural properties of the samples were investigated using the ASAP 2020 equipment, Micromeritics, in the relative pressure range of 10<sup>-5</sup> < P/P<sub>0</sub> < 0.99. Before the analyses, the samples were degassed for 10 h at 300°C in 4.0 μmHg of vacuum. The BET surface area was obtained by the multipoint method in the range of 0.05 < P/P<sub>0</sub> < 0.2, and the surface area of micropores was calculated using the Dubinin-Astakhov equation (DA). The pore size distribution (PSD) was calculated based on the non-local functional density theory (NLDFT) using the slit-shaped pore model.

## 2.2 n-hexane capture tests

Hexane (PA Sigma-Aldrich, 98.5%) was the volatile organic compound used in this study. Capture experiments were conducted via Thermogravimetry using a Shimadzu TG-50 thermal analyzer at atmospheric pressure. Samples (~ 5 mg) were heated at 10°C min<sup>-1</sup> to 150°C for 30 minutes under a flow of 100 mL min<sup>-1</sup> N<sub>2</sub> to remove moisture and adsorbed gases. After cooling to 30-45°C (± 2°C), the nitrogen flow reduced to 50 mL min<sup>-1</sup>, and a gas mixture (100 mL min<sup>-1</sup> total flow) containing VOC vapor in nitrogen (generated at 25°C ± 2°C) was introduced. The vapor quantity was determined using Antoine's equation [5]. VOC concentrations in this work were 6,7; 8,2; 10,0; 12,0; 14,3; 17,0; 20,1; 23,6; 27,6; 34,9 mmol L<sup>-1</sup>. Adsorption isotherm studies were conducted at temperatures of 30, 35, 40, and 45°C, respectively

## 3 Results and Discussion

The nitrogen adsorption isotherms and pore distribution by NLDFT in Figure 1(a) and 1(b), and the textural properties in Table 1, confirm hierarchical pore distribution for the carbons.

The reference material's adsorption isotherm is mainly type I(a), indicating microporosity with a small H4 hysteresis loop, suggesting some mesoporosity. Only 10% of the total pore volume is mesoporous, with 89.7% in the micropore range (< 0.7 nm to 2 nm). This micropore volume is distributed as 38.9% ultramicropores (< 0.7 nm), 16.1% supermicropores (0.7 – 1 nm), and 34.7% micropores (1 – 2 nm)[6].

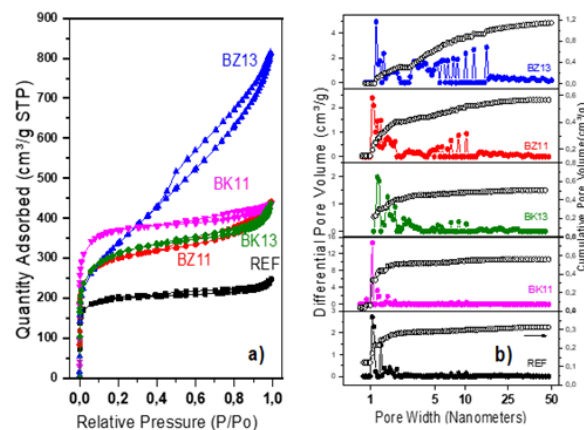


Fig. 1.(a) Nitrogen adsorption/desorption isotherms; and (b) Pore distribution by NLDFT.

Table 1. Textural Properties.

Sample	<sup>a</sup> S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	<sup>b</sup> S <sub>mic</sub> (m <sup>2</sup> g <sup>-1</sup> )	<sup>c</sup> V <sub>T</sub> (cm <sup>3</sup> g <sup>-1</sup> )	<sup>d</sup> n	eV <sub>meso</sub> (cm <sup>3</sup> g <sup>-1</sup> )
REF	701	866	0.4351	1.13	0.0322
BK11	1312	1473	0.5951	1.40	0.0510
BK13	1107	1269	0.7200	1.00	0.0987
BZ11	1032	1261	0.7202	1.00	0.1627
BZ13	1188	1254	1.1473	1.00	0.8414

<sup>a</sup> S<sub>BET</sub>, surface area calculated by the B.E.T. equation at pressure P/P<sub>0</sub> = 0.05-0.2.

<sup>b</sup> S<sub>mic</sub>, surface area of micropores calculated by the DA method

<sup>c</sup> V<sub>T</sub>, total pore volume estimated by the amount adsorbed at pressure P/P<sub>0</sub> = 0.99.

<sup>d</sup> Exponent of the Dubinin-Astakhov equation

<sup>e</sup> Pore volume distribution calculated by the NLDFT method using the slit pore model.

The adsorption isotherms for potassium-activated materials are predominantly type I(b), which are attributed to essentially microporous

materials but with wider pores. The hysteresis loop confirms the presence of pores larger than 4 nm, which can be characterized as H4 type, with pore volume between 9.1% and 19.6% in the mesopore region. The reduction of the BET surface area with the increase in the potassium amount is a result of the chemical attack on the carbonaceous structure, increasing the size of the pores and reducing the area. The materials BK11 and BK13 are mostly microporous, corresponding to a total of 90.9% for BK11 and 80.4% for BK13 in the range < 0.7 to 2 nm. Of this total, the BK11 material has 6.8% of the pores in the region of ultramicropores (< 0.7 nm), 53.2% of supermicropores (0.7 – 1 nm) and 30.9% of micropores (1-2nm). The BK13 material did not present pores for values lower than 0.7 nm, 43% of supermicropores (0.7-1 nm), and 37.4% of micropores (1-2 nm). Potassium activation improves textural properties when compared to REF (BET area of 701 m<sup>2</sup> g<sup>-1</sup>; total pore volume 0.4351 cm<sup>3</sup> g<sup>-1</sup>), BK11 (1.312 m<sup>2</sup> g<sup>-1</sup>; 0.5971 cm<sup>3</sup> g<sup>-1</sup>) and BK13 (1.107 m<sup>2</sup> g<sup>-1</sup>; 0.7200 cm<sup>3</sup> g<sup>-1</sup>).

Activation with zinc also causes an improvement in textural properties compared to the reference (REF). The isotherms are characteristic of type I(b) and a hysteresis loop of H4 type. These are micromesoporous materials with greater contribution in the mesopore range (28.7% of the pore volume). BZ11 carbon is mostly a microporous material, with 71.3% of the micropore volume between < 0.7 – 2 nm. Of this value, 26.8% (< 0.7 nm), 7.8% between 0.7 - 1 nm, and 36.7% between 1 – 2 nm.

The BZ13 material presents strong nitrogen adsorption at low pressures, characteristic of micropores, with the opening of a hysteresis loop at P/P<sub>0</sub> = 0.4 formed by a steep slope tending to infinity, indicating a wide distribution of pores in the mesoporous range. The isotherm changes from the reference material, becoming a type IV(a) according to IUPAC, which is typical of micromesoporous adsorbents but with a greater tendency to the mesopore range. The hysteresis loop is of the H3 type, which is characteristic of materials that do not have their pores fully filled [7]. The material is predominantly mesoporous, with 73.3% of the pore volume in the mesopore range. Of this total, 37.6% of the pores are in the range of small mesopores between 2 – 5 nm and 17.9% between 5 – 10 nm. The increase in the content of ZnCl<sub>2</sub> causes the formation of mostly mesoporous structures by widening the micropores and converting them into mesopores [8]. In addition, activation with zinc

chloride in the hydrothermal step leads to a greater decomposition of cellulose molecules, favoring the formation of high amounts of mesopores and generating better textural properties [9]

The Dubinin–Astakhov exponent provides us with information about the degree of homogeneity of a microporous system, and the value of *n* is between 1 and 4 for carbonaceous adsorbents. For values of *n* less than 2, a heterogeneous distribution of micropores is assigned, and for values of *n* greater than 2 is assigned to carbonaceous solids with homogeneous micropores [9]. All materials produced presented *n* values between 1 and 1.40, showing the degree of heterogeneity of microporous systems. Figure 2 (a) shows the screening of the *n*-hexane capture capacity of the different activated carbons, Figure 2 (b) shows the correlation between adsorption capacity and micropore volume between 1-2nm

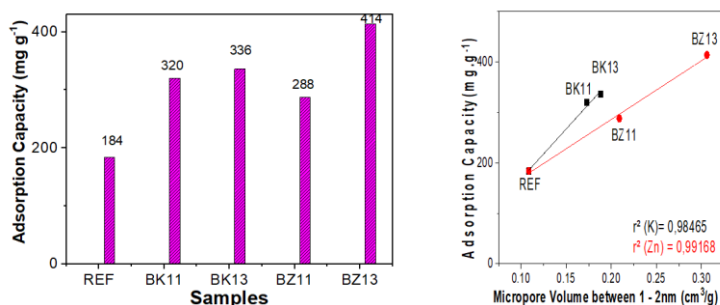


Fig. 2 (a) Screening of *n*-hexane adsorption on activated carbons (b) Correlation Between adsorption capacity and micropore volume between 1-2nm.

In general, all materials showed an excellent performance of the capture capacity of *n*-hexane. The reference material (REF), which is a biochar without activation, was the material with the lowest capture performance of all VOCs. The activation process and the increase in the ratio of activating agent from 1:1 to 1:3 increased the capacity of capturing VOCs of these materials, related to the strong development of the hierarchical porous structure of the activated carbons when compared to the reference material. BZ13 activated carbon stood out, achieving high capture capacities for most VOCs. In the literature, *n*-hexane adsorption is 230 mg g<sup>-1</sup>[9]. Using pore volume distribution calculated by the NLDFT method, one can observe that the capture of VOCs is maximized for high micropore volumes in the 1-2 nm range, Figure 2 (b).

As BZ13 exhibited the best n-hexane adsorption results due to its higher total and mesopore volume, tests were conducted varying n-hexane concentration and adsorption isotherms, as shown in Figure 3(a) and (b).

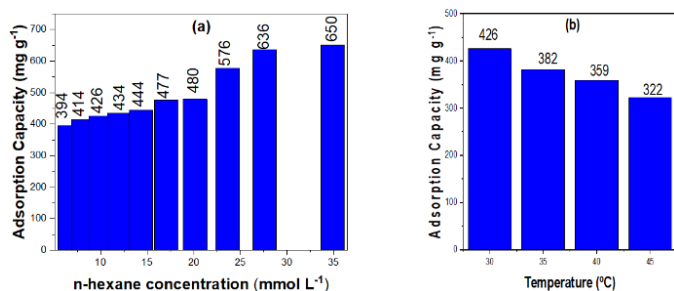


Fig. 3 (a) Study on the Variation of n-Hexane Concentration on BZ13 Carbon (b) Study on the Variation of Adsorption Isotherms

It is observed that as the n-hexane concentration increases, the amount adsorbed rises from 394 to 650 mg g<sup>-1</sup>. With the increase in temperature, the vapor pressure of n-hexane also increases, and the higher the vapor pressure of the VOC, the greater the amount adsorbed[8]. The adsorption capacity decreases from 426 mg g<sup>-1</sup> to 322 mg g<sup>-1</sup> with the increase in temperature from 30°C to 45°C, respectively. This suggests that the capture process is mostly governed by physisorption, which is an exothermic process, reducing its efficiency with increasing temperature [3].

#### 4 Conclusions

The REF, BK11, BK13, and BZ11 materials are predominantly microporous, with Type I(a) isotherms and H4 hysteresis loops, whereas BZ13 is mainly mesoporous, with a Type IV(a) isotherm and H3 hysteresis loop. All produced materials are efficient at capturing hexane, with BZ13 being particularly notable. There is a decrease in the amount adsorbed as the isotherm temperature increases, indicating physisorption and an exothermic process, and an increase in the amount

adsorbed as the n-hexane concentration rises, due to the increase in vapor pressure.

#### 5 Acknowledgements

To CNPq for the granted master's scholarship. To MCTI/FINEP, Advanced Materials and Strategic Minerals 2020 project, approved under Ref. No. 0057/21.

#### 6 References

- [1] Islam N, Saikia BK. An overview on atmospheric carbonaceous particulate matter into carbon nanomaterials: A new approach for air pollution mitigation. *Chem*, 2002, 303, 135027
- [2] Czerwinska N, Giosue C, Matos I, Sabbatini S, Ruello ML, Bernardo M. Development of activated carbons derived from wastes: coffee grounds and olive stones as potential porous materials for air depollution. *Sci Tot Env*, 2024, 914, 169898
- [3] De Andrade RC, Menezes RSG, Fiuza Júnior RA, Andrade HMC. Activated carbon microspheres derived from hydrothermally treated mango seed shells for acetone vapor removal. *Carbon Letters*, 2021, 31, 779-793.
- [4] Jia L, Shi J, Long C, Lian F, Xing B. VOCs adsorption on activated carbon with initial water vapor contents: Adsorption mechanism and modified characteristic curves. *Sci Tot Env*. 2020, 731, 139184.
- [5] Wang G, Dou B, Zhang Z, Wang J, Liu H, Hao Z. Adsorption of benzene, cyclohexane and hexane on ordered mesoporous carbon. *J Env Sci*, 2015, 30, 65-73.
- [6] Thommes M, Kaneko K, Neimark AV, Olivier JP, Reinoso FR, Rouquerol J, Sing KSW. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure AppChem*, 2015, 87, 1051-1069.
- [7] Wu S, Peng H, Xu J, Huang L, Liu Y, Xu X, Wu Y, Sun Z. Nitrogen/phosphorus co-doped ultramicropores hard carbon spheres for rapid sodium storage. *Carbon*, 2024, 218, 118756
- [8] Yang J, Qiu K. Development of high surface area mesoporous activated carbons from herb residues. *Chem Eng J*, 2011, 167, 148-154.
- [9] Heidarnejad Z, Dehghani MH, Heidari M, Javedan G, Ali I, Sillapãa M. Methods for preparation and activation of activated carbon: a review. *Env Che Lett*, 2020, 18, 393-415.