Preparation of porous carbons by KOH activation of different types of biomass for CO_2 adsorption by Temperature Swing Adsorption

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Abstract

Biomass is considered a promising source for the production of functional carbon materials due to their sustainability, low cost, and high carbon content. In this work, yellow mombin seeds (YM), coconut shell (CS), and banana pseudostem (BP) are used to obtain activated carbons (AC) using KOH as activating agent. The activated carbons were obtained through carbonization at 400°C, impregnation with KOH, and chemical activation by pyrolysis at 750°C. The physical chemical properties were studied by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and textural analysis. Adsorption tests were investigated using Temperature Swing Adsorption (TSA) based on adsorption capacity as a function of temperature. The results showed that the AC from these three biomass residues have high surface areas of 924 $m^2 \cdot g^{-1}$ (YM_{KOH}), 767 $m^2 \cdot g^{-1}$ (BP_{KOH}), and 863 $m^2 \cdot g^{-1}$ (CS_{KOH}) and total pore volumes of 0.4991 $cm^3 \cdot g^{-1}$, 0.7051 $cm^3 \cdot g^{-1}$, and 0.4186 $cm^3 \cdot g^{-1}$, respectively. The maximum CO_2 adsorption capacity of the produced activated carbon was 9.1% achieved at a temperature of 30°C for coconut shell derived carbon. These results demonstrate that the AC obtained from these three biomass residues can be effectively used in CO_2 adsorption processes.

Keywords: biomass, activated carbon; CO_2 adsorption, TSA.

1. Introduction

The accelerated growth of industrial processes in the 20th century and the first decades of the 21st century has been sustained by excessive consumption of fossil fuels [1,2]. This growth has been accompanied by an increase in greenhouse gas emissions, negatively affecting the global climate [3]. Among these gases, CO_2 stands out as the main greenhouse gas, deeply involved in climate change and global warming, accounting for approximately 63% of the cumulative temperature impact of all greenhouse gases [4].

Activated carbons (AC) have been efficiently used as solid materials in CO_2 adsorption processes [5,6,7]. However, the synthesis of AC is an expensive procedure, constituting a primary obstacle to their commercialization [8]. Therefore, biomass residues with high fixed carbon content, such as fruit shells or seeds, are being widely used as precursors for more economically viable AC, which reduces the cost of the carbon and the accumulation of residues derived from agro-industrial processes [9 – 12].

Brazil is a major fruit producer, and fruit processing for internal consumption and export generates large quantities of waste, most of which are inadequately disposed, due to their low economic value. In this work, three different biomass residues from fruit production and processing (yellow mombin seeds, coconut shell and banana pseudostem) were used to obtain porous carbons that were evaluated in CO_2 adsorption by the Temperature Swing Adsorption (TSA) method.

2. Materials and Methods

For the production of activated carbons, yellow mombin seeds, banana pseudostem, and coconut shells were used. These materials, which are residues from agro-industrial processes, were collected, washed, dried for three days at a temperature of 100°C, and ground in a knife mill. They were then sieved using a 100-mesh sieve. The obtained materials were carbonized at 400°C in an inert atmosphere with a nitrogen flow rate of 150

mL min^{-1} and a heating rate of 10°C min^{-1}, then impregnated with KOH in an aqueous solution at a mass ratio of 1:1. Next, the aqueous solution was evaporated at 85°C, and the resulting carbon was pyrolyzed in a tubular furnace at 750°C with the same parameters used during carbonization. The pyrolyzed samples were dispersed in an aqueous solution of HCl 1 mol L^{-1} to neutralize excess KOH and dissolve inorganic residues. The samples were subsequently washed with hot deionized water at 85ºC under stirring. The prepared carbons were then filtered and washed with deionized water until pH = 7. Finally, the washed material was dried at 80°C for 12 hours.

The Temperature Swing Adsorption (TSA) method was performed using a Shimadzu DTG-60H thermogravimetric analyzer. Initially, a study of the adsorption capacity of the prepared materials was conducted, and the test program consisted of the following steps: Drying the material at 200°C for 30 minutes under a nitrogen flow (100 mL·min^{-1}); Cooling down to 30°C under a nitrogen flow (100 mL·min^{-1}); introducing a CO_2:N_2 = 1:1 gas mixture for 30 minutes, with a total flow rate of 100 mL·min^{-1}. To obtain precise data, blank tests were performed to avoid artifacts due to the change of the purge gas (N_2) to CO_2/N_2 mixture.

3. Results and discussions

The XRD patterns of all the samples are shown in Figure 1. As seen in the figure, the activated carbon derived from yellow mombin seeds (YM_{KOH}) and that derived from coconut shell (CS_{KOH}) exhibit an amorphous halo with broad peaks at 23.5° and 43.4°, corresponding to the (002) and (100) planes of amorphous graphite carbon, indicating a material with an amorphous structure and disordered graphitic planes [13]. For the carbon derived from banana pseudostem (B_{PKOH}) it was possible to notice the presence of some peaks that were identified as $CaCO_3$ (PDF#01-086-2339). Calcium carbonate was possibly formed by the interaction of CO_2 with calcium present in the biomass residue during pyrolysis.

The morphology of the biochars and AC carbons is shown in Figure 2. The biochars obtained from the biomass at a temperature of 750 °C, Figures 2.a, 2.c, 2.e, exhibit an irregular and rough morphology with shallow cavities. Activation with KOH caused an increase in the roughness of the surfaces of the AC, Figures 2.b, 2.d, 2.f. Additionally, the activation process led to the formation of large deep cavities, which may be linked to the dehydrating capacity that influences decomposition during pyrolysis. In CS_{KOH}, it is possible to observe regular and deep cavities resembling tubes grouped in parallel.

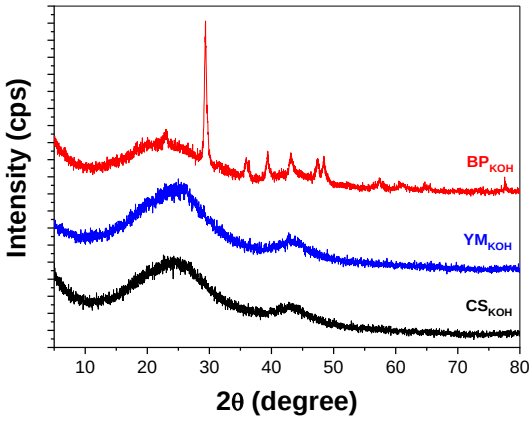


Figure 1. XRD patterns of activated carbons.

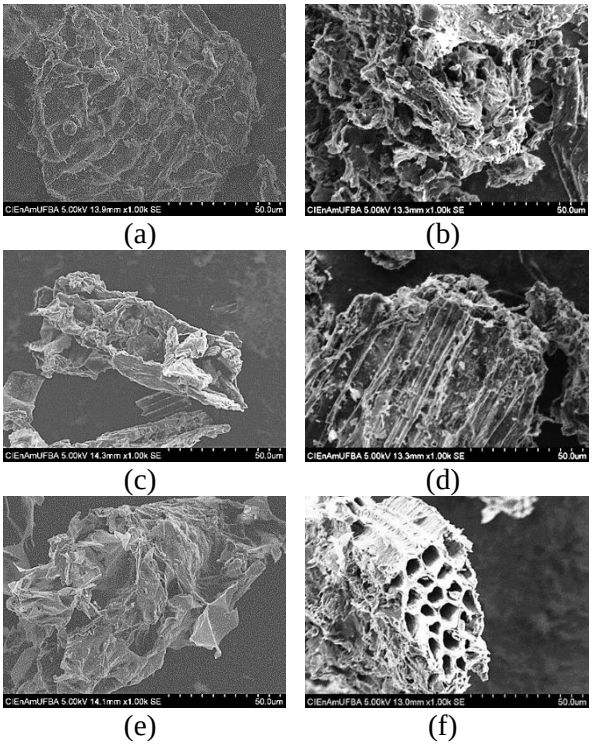
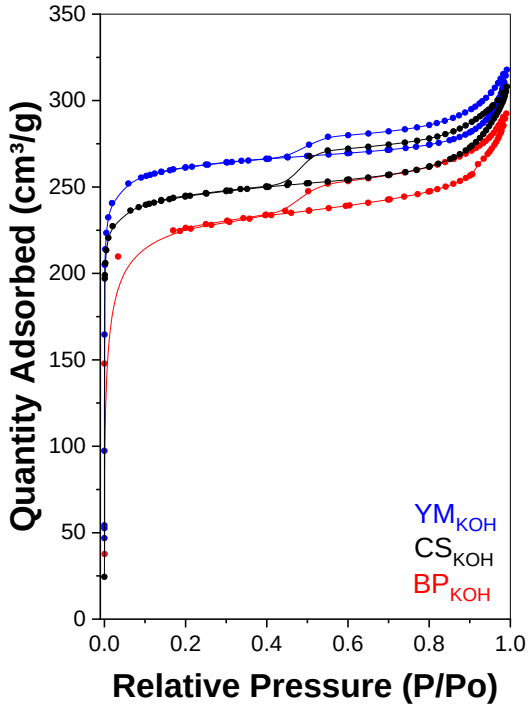


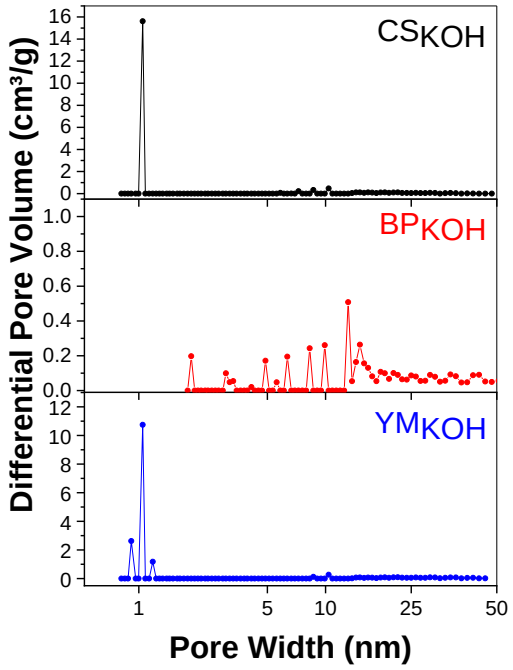
Figure 2. Scanning electron microscopy of the coals: (a) YMSRC, (b) YM_{KOH} (c)BPRC, (d) BP_{KOH} and (e) CSRC, (f)CS_{KOH}.

The results of the textural analysis of the AC are presented in Figure 3 and Table 1. Figure 3.a shows the nitrogen (N_2) adsorption isotherms of the AC, and Figure 3.b displays the pore size distribution obtained by the Non-Local Density Functional Theory (NLDFT) method. According to IUPAC, the AC exhibited predominantly type I adsorption

isotherms transitioning to type IV, which is common in microporous materials with the presence of mesopores, showing a hysteresis loop at P/Po ≈ 0.4, typical of micro-mesoporous materials.



(a)



(b)

Figure 3. (a) Nitrogen adsorption isotherms; (b) Pore distribution by DFT

The N_2 physisorption data were mathematically processed using the Brunauer-Emmett-Teller (BET), Dubinin-Radushkevich (DR), Dubinin-Astakhov (DA), and Non-Local Density Functional Theory (NLDFT) methods, and the resulting textural properties are presented in Table 1

Table 1. Textural properties of the prepared adsorbents.

Sample	S_{BET}[a] (m^2/g)	S_{micro}[b] (m^2/g)	S_{micro}[c] (m^2/g)	S_{NLDFT}[d] (m^2/g)	V_{NLDFT}[e] (cm^3/g)
YM_{KOH}	924	1150.6	1082.6	977.1	0.49908
BP_{KOH}	767	-	-	1071	0.7051
CS_{KOH}	863	1070	1056	953.4	0.4186

[a] Surface area calculated by the BET equation.
[b] Micropore area calculated by the Dubinin-Radushkevich method.
c Micropore area calculated by the Dubinin-Astakhov method.
[d] Surface area calculated by Non-Local Density Functional Theory.
[e] Total pore volume calculated by Non-Local Density Functional Theory.

The results obtained from the study of the CO_2 adsorption capacities of the prepared AC are shown in Figure 4. The results presented in this figure show that the material with the highest adsorption capacity was CS_{KOH} (9.1%), followed by YM_{KOH} (8.4%), and the material with the lowest adsorption capacity was BP_{KOH} (6.3%). This result may be associated with the presence of silicates embedded in the matrix or on the surface of BP_{KOH}

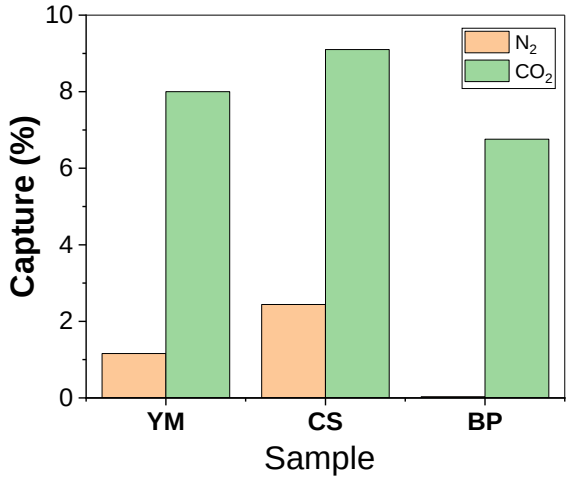


Figure 4. CO_2 and N_2 capture during coadsorption at 30°C (carbon mass ≅ 6.0 mg)

4. Conclusions

This study shows that large-scale biomass residues, such as yellow mombin seeds, coconut

shell, and banana pseudostem, can be used as raw materials to produce activated carbon materials with large surface areas and high pore volumes, using KOH as an activating agent. KOH activation allows for tailoring the properties of activated carbon, such as micropore and mesopore volumes. CO_2 adsorption reached 6.3% to 9.1% at a temperature of 200 °C in a 100 mL·min^{-1} flow of a 1:1 CO_2 and gas mixture. The selected biomasses are mainly composed of cellulose, hemicellulose, and lignin, which are known to be suitable precursors for the production of AC. Therefore, their low cost and wide availability can drive the economical production of activated carbon. Additionally, the presence of graphitic carbon with high mesopore volumes in the AC can facilitate ion diffusion, while the large surface areas and porosities of the activated carbon materials make them suitable for use as adsorbents in adsorption processes through electrical modulation.

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