**Performance of porous carbons based on waste-printed paper on the CO2 capture by Temperature Swing Adsorption**

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**Abstract**

This work evaluates the performance of two porous carbons prepared from waste printed paper in the adsorption of CO2 using the temperature swing adsorption (TSA) method. Activated carbons were obtained through the pretreatment of waste printed paper, impregnation with KOH or K2CO3, and chemical activation by pyrolysis at 800°C. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) were used to analyze the effect of the activating agents on the morphology, composition, and microstructure of the activated carbons, respectively. The nitrogen physisorption isotherms were used to investigate the carbons textural properties and the pore size distribution was calculated using the NLDFT method. The pore formation mechanism under the effect of the two activating agents was also analyzed. Adsorption tests were investigated using TSA based on adsorption capacity as a function of temperature. The results showed that the activated carbons with KOH (AC-KH) and K2CO3 (AC-KC) have high surface areas of 1090 m²·g⁻¹ and 1059 m²·g⁻¹ and total pore volumes of 0.528 cm³·g⁻¹ and 0.425 cm³·g⁻¹, respectively. The maximum CO₂ adsorption capacity at 30°C of AC-KH and AC-KC was 7.35% and 6.14%, respectively. The results indicate that printed paper is a promising low-cost precursor to produce activated carbons for CO₂ adsorption.

*Keywords:* waste, printed paper, activated carbon, adsorção, CO2, TSA

1. **Introduction**

The porous activated carbons is a promising adsorbent that have shown great potential in the treatment of various chemical pollutants [1]. Recent scientific studies have explored the advantages of using activated carbon obtained from paper and cardboard waste instead of traditional non-renewable sources [2 – 5]. This approach reduces environmental impact and valorizes a significant fraction of Municipal Solid Waste, contributing to the sustainable management of natural resources [6, 7].

Pyrolysis and activation were important methods to produce biomass-based porous carbon [8]. The traditional activation methods for pore formation are mainly physical activation and/or chemical activation [9, 10]. Chemical activation refers to the process of using an activating agent to develop the internal structure of carbon materials and eventually forming a large number of pores [11]. Compared to physical activation, chemical activation has the advantages of simple operation, higher yield, lower energy consumption, and large specific surface area [12]. Therefore, the preparation of porous carbon by chemical activation is an economical and feasible method.

In this work, porous carbons were prepared from printed cardboard waste as the carbon precursor using the chemical activation method with KOH or K2CO3 as activating agents. The effect of the two activating agents on the properties of the porous carbon was investigated. This study provides initial experimental results for using porous carbons made from printed paper waste in CO2 adsorption processes.

1. **Materials and Methods**

The pretreatment of printed paper was carried out in three stages. In the initial stage, the shredded paper was soaked in deionized water at 70°C and subjected to magnetic stirring for 240 min, then centrifuged. Next, the obtained pulp was submerged in an aqueous ethanol solution at 50% and 60°C, and again subjected to magnetic stirring for 240 min. In the third stage, the pulp was vacuum filtered to obtain paper pulp, which was dried at 100 °C for 6 h and shredded again to obtain powdered material. After the pretreatment, the powdered material was chemically impregnated in an aqueous solution using KOH (AC-KH) or K2CO3 (AC-KC) as activating agents in a 1:1 mass ratio. Then, the aqueous solution was evaporated, and the impregnated material was pyrolyzed in a tubular furnace at 800°C in a nitrogen flow rate of 150 mL min-1 and a heating rate of 10°C min-1. The activated carbon was subsequently washed with a 0.1 mol L-1 HCl solution and deionized water at 80°C to neutralize and remove inorganic residues. Afterward, it was washed with deionized water at room temperature until a neutral pH was reached. Finally, the material was dried at 80°C for 12 hours.

Scanning Electron Microscopy (SEM), Fourier transformed Infrared Spectroscopy (FT-IR), and X-Ray Diffraction (XRD) were used to analyze the effect of the activating agents on the morphology, composition, and microstructure of the activated carbons, respectively.

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: (i) drying the material at 200°C for 30 minutes under a nitrogen flow (100 mL·min-1); (ii) cooling down to 30°C under a nitrogen flow (100 mL·min-1); and (iii) introducing a CO2:N2 = 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 (N2) to CO2/N2 mixture.

**3. Results and discussions**

Figure 1 presents the results of both XRD and FTIR experiment. Figure 1.a shows that both activated carbons exhibit two broad peaks with relatively low intensities at 2θ values around 23.19° and 43.5°, corresponding to the (002) and (101) reflections of partially graphitic domains in a typical amorphous carbon [3, 13]. This suggests that activation with KOH or K2CO3 promotes the formation of defects and an amorphous structure. The shift of the peak corresponding to the (002) reflection to a lower diffraction angle, 23.19° compared to 26.3° in graphite, indicates an increase in the interlayer spacing in the carbon [13].

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| (a) | (b) |
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Figure 1. Printed-paper activated carbons: a) X-ray diffraction patterns; b) FT-IR spectra.

From the FT-IR spectra of the activated carbons AC-KH and AC-KC presented in Figure 1.b, the presence of the OH functional group connected by hydrogen bonds is observed in the band with wavelengths of 3300-3500 cm-1. The bands around the wavelengths of 1750-1700 cm-1 and 1600-1500 cm-1 are associated of the C–O corresponding to the asymmetric stretching and C=C attributed to the stretching in the aromatic ring structure, respectively. The frequency band in the range of 1000-1300 cm-1, corresponding to the C=O groups, relates to the stretching vibration of the carbon skeletal structure.

Nitrogen isotherms are presented in Figure 2. Both materials exhibit a relatively high amount of nitrogen adsorption, evidencing the porous nature of carbon. A large amount of nitrogen adsorption at low pressure indicates that these materials are predominantly microporous, but AC-KH presents a type H4 hysteresis loop, according to IUPAC [14], which suggests an important contribution of mesoporosity in this sample and, therefore, a characteristic of hierarchical porous material. A type H4 hysteresis is indicative of the presence of slit-shaped mesopores created in the carbon layer during the high-temperature activation step (Figure 2.a).

The activation of paper-treated residues with potassium carbonate caused strong reactions with the carbonaceous structures, inducing the oxidation of carbon to CO2 and breaking structures, thus promoting microporosity. The pore volume distribution in AC-KC activated with K2CO3 is concentrated in the micropore range, with a slight amount of mesopores, as can be observed in Figure 2.b.

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|  |
| (a) |
|  |
| (b) |

Figure 2. (a) N2 adsorption-desorption isotherms on the activated carbons; b) Pore size distribution by NLDFT method.

Textural properties calculated from the nitrogen-physisorption isotherms were calculated and are shown in Table 1.

Table 1. Textural properties of the prepared adsorbents.

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| **Sample** | **SBETa****(m2/g)** | **Smicb****(m2/g)** | **Vtc****(cm3/g)** | **Vmicd****(cm3/g)** | **Vmesoe****(cm3/g)** |
| AC-KH | 1190.1 | 1328.8 | 0.528 | 0.440 | 0.088 |
| AC-KC | 1058.5 | 1309.7 | 0.425 | 0.396 | 0.029 |

a BET surface area: b Smic, surface area calculated by DA method; c Vt, total pore volume estimated by NLDFT method.8; d Micropore volume estimated by NLDFT; e Mesopore volume estimated by NLDFT.

It can be observed that ACPKH and ACPKC have BET surface areas of 1090.1 m²·g-1 and 1058.5 m²·g-1 and large pore volumes ranging from 0.528 cm³·g-1 to 0.425 cm³·g-1, respectively. As can be seen, the results obtained with the two activating agents, KOH and K₂CO₃, are quite close, with the BET surface area and total pore volume of the AC-KH activated carbon being slightly higher.

The morphology of the activated carbons is shown in Figure 3. A porous network structure with many cavities and high surface roughness is observed for both samples.

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| Foto em preto e branco  Descrição gerada automaticamente (a)  | Foto em preto e branco  Descrição gerada automaticamente (b)  |

Figure 3. Scanning Electron Microscopy of the activated carbons a) Activate carbon ACPKH; b) Activate carbon ACPKC.

The pore formation mechanism in ACPKH can be attributed to the oxidation and reduction reaction of C with KOH and the gasification with release of H2, H2O, CO, and CO2. Additionally, metallic K is intercalated into the carbon matrix due to KOH during the pyrolysis process and reacts with C; after the removal of metallic K and other K compounds, a porous structure can be observed.

For the sample AC-KC pore formation mechanism is attributed to the fact that at the activation temperature of 800°C, K₂CO₃ decomposes into K₂O and CO₂, which, during the activation process, can corrode the carbon structure, thereby promoting the formation of a porous structure.

The results of the CO2 adsorption capacity tests of the activated carbons AC-KH and AC-KC are shown in Figure 4.

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Figure 4. CO2 capture (%) at atmospheric pressure and 30°C; mass = 6 mg; β = 10 °C·min-1, F = 100 mL·min-1 (50% CO2 + 50% N2).

According to the results presented in the Figure 4, it can be observed that the activated carbon with KOH shows the best CO2 adsorption effect, with 7.35% under the tested conditions, superior to the 6.14% adsorption obtained with the activated carbon with K2CO3. This result is associated with the AC-KH structure, which has a larger micropore area (Smic = 1328.8 m²·g-1) and a greater micropore volume (0.440 cm³·g-1).

**4. Conclusions**

The results of this study show that porous activated carbons prepared from paper waste can be produced through pre-treatment, chemical activation, and pyrolysis, reducing the traditional carbonization before activation, which reduces the energy consumption of the preparation method by two phases. Using KOH and K2CO3 allows the properties of activated carbon to be adapted, such as micropore and mesopore volumes. The results showed that activated carbons AC-KH and AC-KC made from printed paper waste reached an adsorption capacity of 7.35% and 6.14% at a temperature of 30 °C in a flow of 100 mL·min⁻¹ of a mixture 1:1 of CO2 and N2. In general, activated carbons from waste paper obtained using the methodology used in this work show high porosity and have good CO2 adsorption performance through temperature modulation and potential for further improvements. This work can provide a useful reference for developing solid CO2 adsorbents using different types of paper contained in solid waste.

**Acknowledgments**

The authors thank to FINEP project USINA (ref. 0057/21) for the financial support.

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