

Activated Carbon from Olive Stone for CO₂ Capture

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Abstract— three type of activated carbon were prepared in this study from olive stone. The first type was prepared by chemical activation using phosphoric acid, the second type was prepared by physical activation using water vapour and the third was produced by combined of the both precedent methods. All samples were chemically characterized by TPD-MS and the porous texture was evaluated from the N₂ and CO₂ adsorption isotherms at -196 and 0°C respectively. The CO₂ adsorption capacities of the adsorbents were evaluated at 25 and 100°C in a thermogravimetric analyser.

Keywords— Activated Carbon, Olive stones, CO₂ Capture

I. INTRODUCTION

Activated carbon is a commercial adsorbents, which can be prepared from a variety of raw materials such as coal (lignite, bituminous), fruit shells (almond, coconut), fruit stones (olive, cherry), wood (sawdust), peat, etc. [1] Activated carbon characterized by high specific area and tunable porosity find utility in many vital technologies namely energy storage (super capacitors, batteries, hydrogen sorption, methane storage [2]) and CO₂ capture. Activated carbon can be prepared by chemical or physical activation. In chemical activation, the precursor is carbonised in the presence of chemical agent (KOH, NaOH, H₃PO₄, K₂CO₃, ZnCl, etc). This method need another additional step to eliminate the excess of activating agent incorporated in the product. On the other hand, physical activation has a lower environmental impact, as it uses CO₂, H₂O or air as activating agent. This study was an attempt to produce activated carbon as low cost materials for CO₂ capture. To reach this objective, three type of activated carbon have been prepared from olives stones.

II. EXPERIMENTAL

A. Preparation of activated carbon

The three type of Activated carbon were prepared from olive stones. The raw material was washed with distilled water to eliminate the impurities and then dried at room temperature.

So to prepare the chemical activated carbon noted 'CH450' olive stones were firstly impregnated with phosphoric acid solution (50wt. %) at 110°C for 9 h. Then the dried solid was

subjected to thermal activation in a nitrogen atmosphere in a horizontal tubular reactor at 170°C for 30 min and at 450°C for a reactive time of 2.5 h.

Combined activated carbon noted CO390 was prepared by impregnation of olive stones with phosphoric acid at the same condition that the first product. Then the dried solid was subjected to thermal activation in a nitrogen atmosphere + water vapor in a horizontal tubular reactor at 170°C for 30 min and at 390°C for a reactive time of 2.5 h.

The preparation process of physical activated carbon noted PH850 consists in the carbonization of the olive stone under nitrogen atmosphere followed by physical activation using water vapor. Carbonization was performed in the presence of a continuous flow of purified nitrogen gas with a flow rate of 10 nL/h. The precursor is heated from room temperature to 600 °C (5 °C/min) and maintained at this final temperature during 60 min. The activation of the obtained char is then realized at 850 °C (the ramp used is 15 °C/min) under 70 vol. % H₂O in N₂ during 360 min, with a total gas flow rate equal to 10 NL/h.

B. Characterization

The carbons obtained were characterized by physical adsorption of N₂ and CO₂ at -196°C and 0°C respectively using a volumetric apparatus. Prior to the measurements the samples were evacuated overnight at 100°C.

The specific surface area was evaluated from the N₂ adsorption isotherms by the Brunauer-Emmett-Teller (BET) equation. The V_p (total pore volume) was assessed from the amount of adsorbed nitrogen at relative pressure of 0.99.

The V_{DR}(micropore volume) and W₀ (narrow micropore volume) were estimated by the Dubinin-Radushkevich method from the N₂ and CO₂ adsorption isotherms, respectively.

The TPD tests were carried out in a thermogravimetric analyser coupled to a FTIR spectrometer. A flow rate of 50 cm³min⁻¹ of Ar and heating rate of 15°Cmin⁻¹ up to maximum temperature of 800°C were used.

The CO₂ capture capacity of the adsorbents was evaluated in a Setaram TGA 92 thermogravimetric analyser, which recorded the mass uptake of the samples when exposed to a gas steam containing (90% of N₂+ 10% of CO₂). Prior to the CO₂ adsorption test, samples were dried in Ar at 100°C for 1h.

III. RESULTS AND DISCUSSION

A. Textural characterisation

As shown in Fig 1, all activated carbons presented type –I adsorption isotherms indicating microporous materials. The amount of nitrogen adsorbed presented a sharp increase at low relative pressure meant that more micropore were presented.

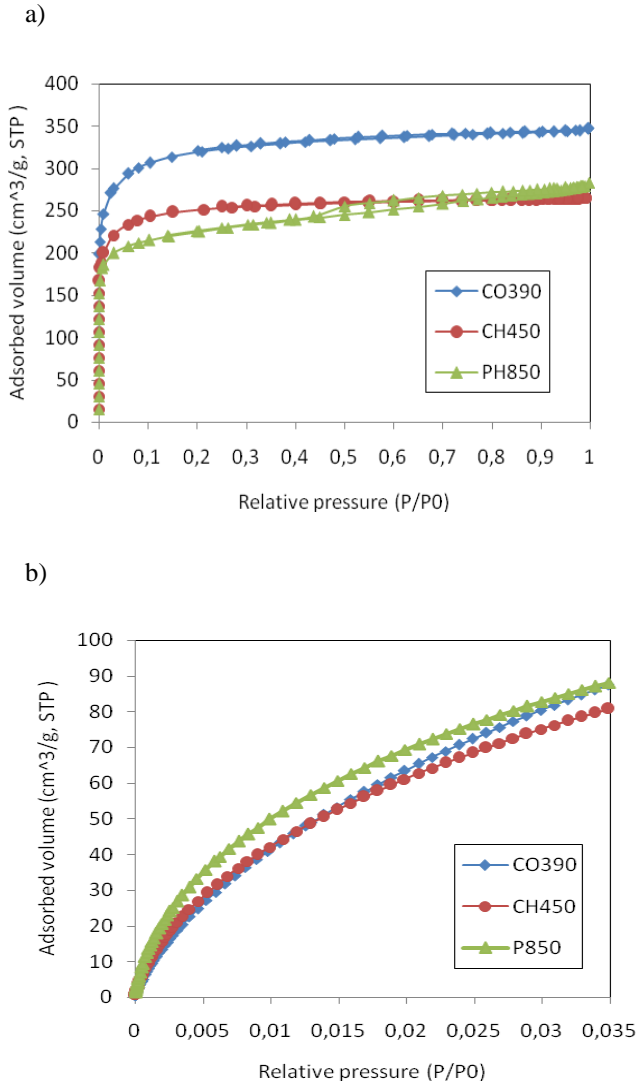


Fig. 1 Adsorption isotherms of Activated Carbon (a) N₂ at -196°C and (b) CO₂ at 0°C.

TABLE I
CHARACTERISTICS OF POROUS TEXTURE FOR ACTIVATED CARBON
DETERMINED FROM N₂ AT -196°C AND CO₂ AT 0°C.

| Samples | S _{BET} (m ² /g) | S _{mic} (m ² /g) | L (nm) | E ₀ (Kj/mol) | W ₀ (cm ³ /g) |
|---------|--------------------------------------|--------------------------------------|--------|-------------------------|-------------------------------------|
| CO390 | 1220 | 673 | 0.73 | 26.16 | 0.246 |
| CH450 | 978 | 685 | 0.67 | 27.54 | 0.229 |
| PH850 | 866 | 780 | 0.60 | 29.36 | 0.234 |

Table 1 gives the characteristics of porosity in activated carbon. These samples show high BET surface area in the range 866-1220 m²/g.

B. TPD-MS

To study the nature of the functional groups present on the surface of the samples, temperature programmed desorption tests were carried out. Fig.2 shows the profiles of evolved CO₂ and CO for samples, in the course of heating at 15°C min⁻¹ in 50 cm³ min⁻¹ of Ar.

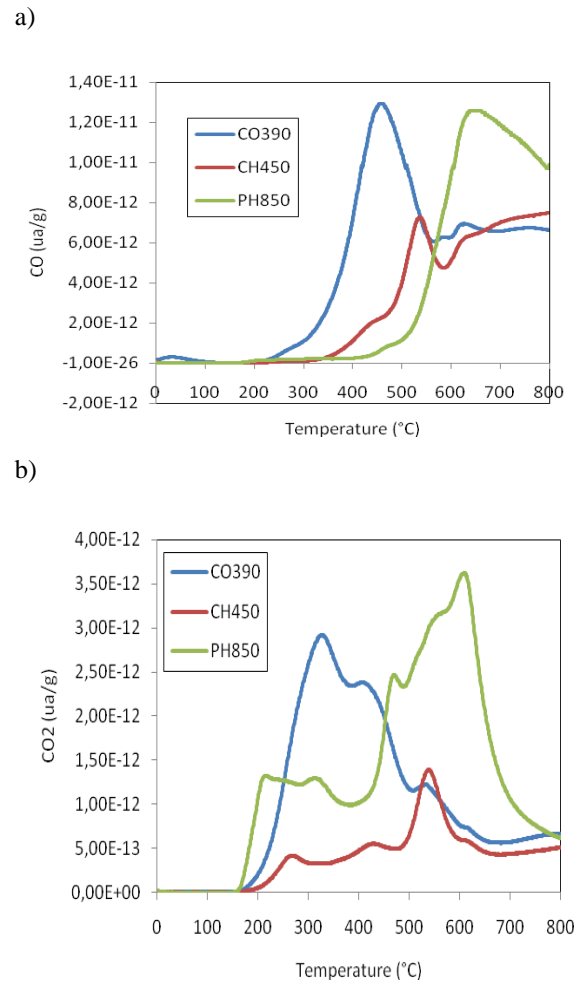


Fig. 2 TPD Spectra for Activated carbon (a) CO evolution, (b) CO₂ evolution

CH450 present the lower CO and CO₂ emissions than the other Activated Carbon, because these others were activated with steam.

The CO profile of PH850 presents a maximum at 630 which may be related to quinone. [3]

CO390 and PH850 present two maxima in the CO₂ profile: at around 350 and 700°C. Low temperature CO₂ is commonly attributed to the decomposition of carboxyls, while higher temperature CO₂ is associated to the decomposition of lactones or anhydrides. [4]

C. CO₂ Capture

Fig.3 gives the CO₂ capture capacities of the samples at 25 and 100°C. Obtained at 1 bar in a binary mixture containing 10% of CO₂ in N₂.

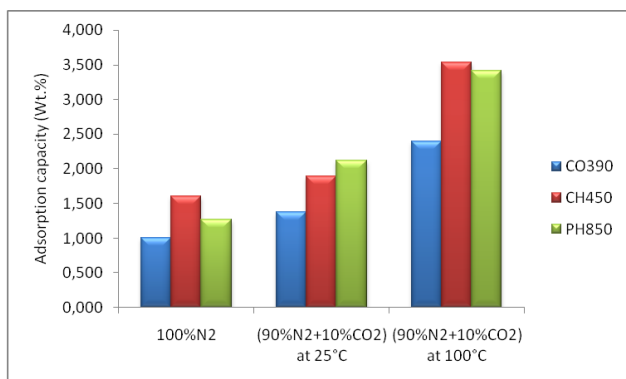


Fig. 3 CO₂ capture capacity evaluated in a thermogravimetric analyser at 1 bar and 10% CO₂ in

The CO₂ uptakes are expressed in terms of mass of CO₂ per mass of dry adsorbents. The adsorption capacity of the activated carbons increases with increasing adsorption temperature. At 25°C, CO₂ capture capacity reaches a value of 2 wt. % for activated carbon PH850. On the other hand, at 100°C this is the activated carbon CH450 who reaches the maximum value of CO₂ uptake which is 3.5wt. %. The values obtained in this study are of the same order as the values found in the work of [5]

IV. CONCLUSIONS

Three type of activated carbon were prepared in this study as low- cost adsorbents for CO₂. All the samples were marked by a microporous texture. The highest BET surface area was found for the activated carbon CO390 which reached 1220 m²/g. The CO₂ capture increase with the increasing of adsorption temperature to reach the maximum at 100°C as 3.5wt.% for CH450 sample. Finally, this work reveals a promoters results and open interesting perspectives for application of activated carbon in CO₂ capture.

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