

# STUDY OF DEVELOPMENT OF THE PORISITY OF THE ACTIVATED CARBON FOR ELIMINATION FROM AN ORGANIC POLLUTANT IN AQUEOUS SOLUTION.

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## Abstract

An agricultural waste, the olive stones, was successively undergone a chemical activation by  $ZnCl_2$  (coals CZ), a physical activation by  $CO_2$  (coals CP) and a combined activation by  $ZnCl_2$  following by  $CO_2$  (coals CC) in order to produce activated carbons for there application in the polluted water treatment. The obtained results show the larger the ratio of  $ZnCl_2$  to olive stones (coals CZ and CC) and the duration of preservation of  $CO_2$  (coals CP), the more developed the porous texture. These results are confirmed by immersion calorimetry in cyclohexane and tri-2,4-xilyl phosphate. Furthermore, the adsorption capacities of the activated carbons obtained by combined activation (coals CC) towards the phenol were the largest.

**Key words:** activated carbon, adsorption, phenol.

## Introduction

Manufacturing activated carbons involves two steps: the carbonization of raw carbonaceous materials in an inert atmosphere and the activation of carbonized product. The carbonization consists of a thermal decomposition of the carbonaceous material, eliminating non-carbon species and producing a fixed carbon mass with a rudimentary pore structure. Very fine and closed pores are created during this step, the purpose of activation is to enlarge the diameters of the fine pores and create new pores. The activation can be carried out by chemical or physical means. In chemical activation, the carbonisation and activation are accomplished in a single step carrying out decomposition of the raw material impregnated with certain chemical agents. The advantages of chemical activation are low energy cost due to lower temperatures (< 800°C) than those needed for physical activation, and high product yields. The physical activation involves gasification of the char (obtained from carbonization of the raw material) by oxidation with steam, carbon dioxide, air or any mixture of these gases in the temperature range 800 to 1100°C. The zinc chloride is one of the chemical activating agents used in the preparation of activated carbon (Hussein and al., 1996). Activated carbons with high apparent surface areas and pore volume were obtained from treatments with potassium hydroxide, zinc chloride, of

anthracite, cloths and some lignocellulosics precursors (Lozano–Castello and al., 2001). For a very long time, activated carbons have been widely used for the removal of organic pollutants from waste waters and drinking water, due to its large surface area and pore volume. The objective of this study relates to the valorisation of a lignocellulosic compound, an agricultural waste, the olive stones. For this purpose, the raw material was successively chemically activated by zinc chloride, physically activated by carbon dioxide and activated by zinc chloride following by carbon dioxide (combined activation) in order to produce activated carbons for its application in the polluted water treatment.

## Experimental

### Preparation of activated carbons

For the chemical activation, the homogeneous mixture of the olive stones and the zinc chloride with different ratios (0.5, 1 and 2 g of  $ZnCl_2$  for 1 g of precursor) is carbonized under a nitrogen flow at a rate of  $5^\circ C/min$  at  $800^\circ C$  and maintained during one hour at this temperature. The obtained carbon is then treated by a hydrochloric acid diluted solution by refluxing during three hours then washed with boiling distilled water until the total elimination of chlorides. In relation to physical activation, the powder of olive stones is carbonized in the same conditions as previously (without landing of 1 h); the nitrogen is then substituted by the carbon dioxide during various durations (1, 2 and 3 h); after cooling under a nitrogen flow, the obtained material is washed in distilled water then oven-dried at  $120^\circ C$  during 3 hours. Finally, the combined activation is applied as follow: the mixture precursor–zinc chloride is treated in the same conditions as in chemical activation (without landing of 1h); the nitrogen is then switched to the carbon dioxide during 1 hour at  $800^\circ C$ . After cooling under nitrogen stream, the resulting carbon is washed in the same conditions as in chemical activation.

### Nitrogen adsorption–desorption and immersion calorimetry

The textural characterization of the prepared activated carbons was performed by nitrogen adsorption and immersion calorimetry techniques. The nitrogen adsorption–desorption isotherms were measured using an automatic adsorption volumetric apparatus (ASAP 2010 of Micromeritics). Microporosity was also studied by immersion calorimetry in a Calvet calorimeter (Calvet using bulb method of fragile point (Robert, 1972), in two liquids (cyclohexane and tri-2,4-xilyl phosphate).

### Adsorption of phenol

The phenol adsorption isotherms on various activated carbons are made at different phenol concentrations with a regular agitation during 24 hours at  $25^\circ C$ . The measurement of the adsorbate concentrations was determined by UV–Visible Spectrophotometer (JASCO V–530).

## Results and discussion

### Characterization of the activated carbons

The nitrogen adsorption–desorption isotherms corresponding to three modes of activation (chemical, physical and combined) are represented in figures (1-a), (1-b) and (1-c).

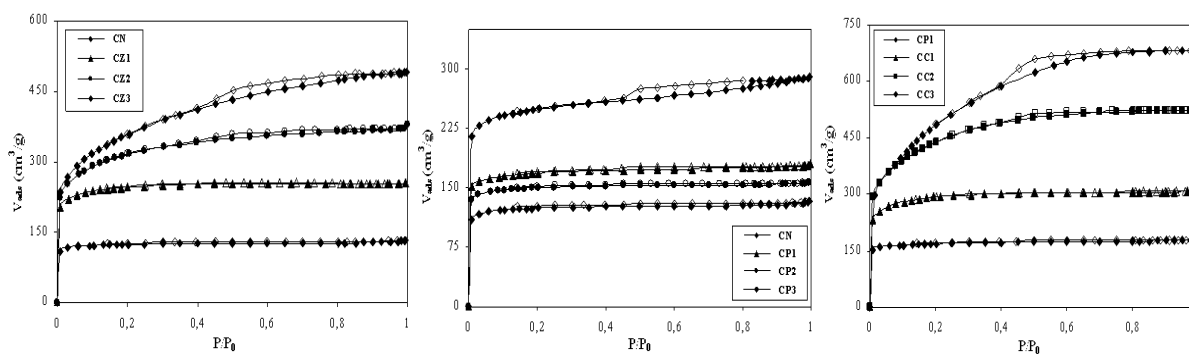


Figure 1: Adsorption–desorption isotherms of  $N_2$  on activated carbons prepared by: (a) chemical activation, (b) physical activation and (c) combined activation.

Figures (1-a), (1-b) and (1-c) show that all nitrogen adsorption–desorption isotherms on various coals are in type I, according to the classification of the IUPAC (IUPAC, 1985); these materials are then essentially microporous, except for CZ3, CP3 and CC3 for which we observe an hysteresis loop of type H<sub>4</sub>, characteristic of capillary condensation phenomenon consecutive to the presence of slit-like mesopores. The larger the ratio of  $ZnCl_2$  to olive stones (coals CZ and CC) and the duration of preservation of  $CO_2$  (coals CP), the more developed the porous texture.

### Adsorption of phenol

The phenol adsorption isotherms on activated carbons prepared by chemical, physical and combined activation of olive stones are represented in figures (2-a), (2-b) and (2-c), respectively.

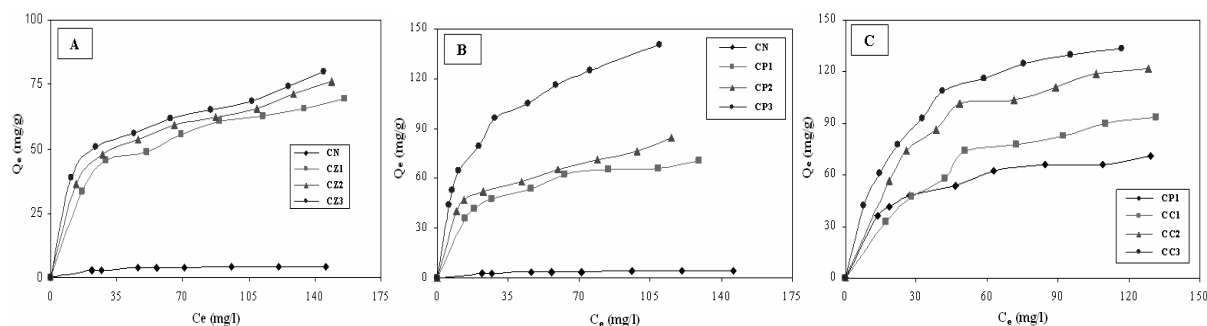


Figure 2: Adsorption isotherms of phenol onto activated carbons obtained by: (a) chemical activation, (b) physical activation and (c) combined activation.

From these results, one observes that the maximal of phenol adsorption capacity,  $Q_0$ , is more raised on combined activation coals (CC1, CC2 and CC3) and on the  $\text{CO}_2$  (3 hours) activation coal CP3; this can be explained by the development more important of the porous textures (wider diameter of pores) during the activation process.

#### 4- Conclusion

This work relates to the preparation of activated carbons from an agricultural waste, the olive stones. At first, we proceed to the activation of the olive stones by various methods of activation (chemical, physical and combined) in order to (with the aim of) develop the porosity of these materials. The second part of this study was devoted to the textural characterization of the resulting materials using nitrogen adsorption and immersion calorimetry techniques. The obtained results show of one part that the porous texture of activated carbons is more developed in the case of combined activation, as the ratio of the activating agent,  $\text{ZnCl}_2$ , is more greater; for example, the BET specific surface area of the coal CC3 reaches a value of  $1793 \text{ m}^2/\text{g}$ . The activated carbons adsorption capacity is determined towards an organic pollutant, the phenol. All phenol adsorption isotherms on various activated carbons are modelled by Langmuir equation. The larger adsorption capacities of phenol were obtained with coals obtained by combined activation, CC3, CP3, CC2 and CC1, ie, 158.7, 156.3, 147.5 and 126.6 mg/g, respectively.

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