

## Use of Activated Carbons for Treatment of Water Polluted by the Phenolic Substances

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The activated carbons of different structures were prepared from a drift lignocellulosic of an Algerian jujube shells. The used precursors were heated at 475, 650 and 800°C, in presence of an activating chemical agent. The porosity characterization of the activated carbons obtained, was investigated by BET method. Their application to the environment was studied for the treatment of polluted water by the phenol and the *p*-cresol. The influence of various parameters such as agitation time, phenolics concentrations, pH and temperature was studied. The Langmuir model was used to describe the experimental results. The results show the role, of the activating chemical agent in the porosity development of materials, by increase of their power adsorbent. It was found that more than 90 % of the phenolic products used in water as pollutants were eliminated by activated carbons. The adsorption was maximum in the pH range 6.2-6.8. The negative values of  $\Delta H$  confirm the exothermic nature of adsorption.

**Key Words:** Drift lignocellulosic, Activated carbon, Activation, Adsorption, Phenolics.

### INTRODUCTION

The pollution is an unfavourable modification of the natural habitat. This modification can affect man directly or through resources by deterioration of the environment. The problem of pollution of waters and mixing of industrial wastewaters to waters used of urban origin, the use of manures and the excess of the pesticides in agriculture permitted the polluting substances in the middle receptor (river, sea, *etc.*). The phenol that is classified as organic pollutant becomes the most toxic organic pollutant<sup>1,2</sup>.

The present technological needs require the adsorbent materials, among them they appear the carbon materials with great adsorbent power, there are the most porous corps known on this day<sup>3</sup>. The activation develops the porous precursor's structure that becomes the primordial characteristic of the adsorbent materials activated carbons.

Nowadays, the activated carbons find numerous applications, in particular in pharmacology, adsorption of gases. On one hand toxic substances that can be found at the state of traces in water and the gold recuperation. On the other hand, for phenolic compounds, they are highly toxic and generally not amenable to biological degradation<sup>4,5</sup>. New methods for treating such effluents are continuously modified and developed.

The proposed methods including chemical oxidation, coagulation, solvent extraction, liquid membrane permeation and adsorption. Among these techniques, adsorption is the most practical method for an overall treatment, especially for effluents with moderate and low concentrations. The utilization of an activated carbon in an imparted process is conditioned by adsorption characterizations, that has great specific surface and existence of microporosity<sup>6</sup>.

The originality of this work is the elaboration and characterization of carbon materials to great adsorption power of liquids and gases. These materials are basis of drifts lignocellulosic, the jujube shells, an abundant agricultural products. Later were carbonised between 650-800°C in presence/or without of a chemical agent (ZnCl<sub>2</sub>) and physical activation with carbon dioxide<sup>8</sup>. The characterization of the porosity by the BET method for adsorption of nitrogen at (-196°C)<sup>7</sup> has been reported earlier.

In order to study the performance of the activated carbons, many experiments were carried out and capacities, the kinetics of adsorption of phenol (P) and *p*-cresol (PC) from water were examined. The influence of several operating parameters, such as pH, contact time, initial concentrations and temperature on the adsorption capacity were investigated. The Langmuir model was used to analyze the adsorption equilibrium<sup>9</sup>.

## EXPERIMENTAL

### Preparation and characterization of the activated carbons

The jujube shells collected from nearby locality was first washed with distilled water to remove the water-soluble impurities and surface adhered particles and then dried at 110°C to remove volatile impurities. Then the precursor was ground in the ball mill sieved to a particle size range of 500-1000 µm.

Four activated carbons were obtained from lignocellulosic material, the jujube shells; (i) **Activated carbon CAI**: By pyrolysis at 800°C for 2 h in inert atmosphere (ii) **Activated carbon CAII**: By physical activation of the sample with CO<sub>2</sub> gazes at 800°C for 2 h (iii) **Activated carbon CAIII**: Chemical activation of the precursor was done with ZnCl<sub>2</sub>, under standard condition ( 50 wt %) and heated at 650°C for 2 h, without soaking time, (iv) **Activated carbon CAIV**: By mix activation, the precursor was impregnated with ZnCl<sub>2</sub> under standard condition (50 wt %) and heated at

650°C, following by carbonization with CO<sub>2</sub> gases at 800°C for 2 h. For all these precursors the pyrolysis was in inert atmosphere.

A volumetric Accersob (Micromeritics) surface analyzer was used to measure nitrogen adsorption isotherm at (-196°C) with a precision of 4 %. Before measurement, the samples were dried in the range 100-110°C and degassed at 150°C under vacuum pressure 10<sup>-4</sup> Pa, during 15 h. The specific surface areas were calculated for activated carbons by the BET (Brunauer-Emmett-Teller) method assuming that the surface area occupied by per physisorpted nitrogen molecule was 0.162 nm<sup>2</sup>. The total pore volumes were estimated to be the liquid volume of N<sub>2</sub> at relative pressure (P/Po) of 0.96. The average poreradius were estimated from BET surface area and total pore volume assuming an open-ended cylindrical pore model without pore networks and from BJH (Barret-Joymer-Halenda)method<sup>10</sup>.

### Procedures for phenolic compounds adsorption experiments

Two solutes, phenol and *p*-cresol were analytical reagent grade (Merck). The aqueous phase for adsorption was prepared by dissolving adequate quantities of compound phenolics in double distilled water and the pH of solutions was measured, the initial pH was about 6.0 for 75 mg/L of phenol and 6.3 for 75 mg/L of *p*-cresol. Table-1 shows some physical characteristics of phenolic compounds.

TABLE-1  
PHYSICAL CHARACTERISTICS OF PHENOLIC COMPOUNDS

Compound	m.w. (g/mol)	m.f.	Purity (%)	Solubility at 293 K g/100 g H <sub>2</sub> O	pK <sub>a</sub> at 298 K
Phenol	94.11	C <sub>6</sub> H <sub>5</sub> OH	73	9.3	9.96
<i>p</i> -Cresol	108.14	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	98	2.3	10.17

In the adsorption equilibrium experiments, 0.1 g carbon were well dispersed in 0.1 L aqueous solution of different initial concentration in the range of 2-75 mg/L, in a 0.25 L flask and stirred for 2 d in a water bath. All the adsorption experiments were carried out at a temperature of 25°C, constant agitation speed (110 rpm). After filtration with glass fibers, the concentration of solutes in the aqueous phase was determined with a Jasco UV/Visible spectrophotometer (700). The selected wavelength was 269 nm for phenol and 276 nm for *p*-cresol. Each experiment was repeated three times under identical conditions. The amount of adsorption at equilibrium, Q<sub>e</sub> (mg/g), was calculated according to eqn. 1:

$$Q_e = \frac{(C - C_e)V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial equilibrium concentrations (mg/L) respectively of phenol and *p*-cresol in solution,  $V$  is the volume in litre (L) and  $W$  is the weight in grams (g) of adsorbent.

The contact time and other conditions were selected on the basis of preliminary experiments, that was demonstrated after 2 h for 75 mg/L at 25°C. The sorption studies were also carried out at 25, 35, 45 and 60°C to determine the effect of temperature and evaluated the sorption thermodynamic parameters.

The effect of pH on the adsorption of phenol (75 mg/L) and *p*-cresol (75 mg/L) on selected carbon at 25°C and for 10 h and constant agitation speed (110 rpm) was examined. The pH values in the range (1-12) were adjusted with dilute HCl (0.1N) and NaOH (0.1N) solutions.

## RESULTS AND DISCUSSION

### Pore structure of the prepared activated carbons

Fig. 1 shows the adsorption isotherms of nitrogen on the prepared activated carbon. It was found that increasing ratio ( $P/P_0$ ) for activated carbons led to increase the volume adsorbed by each precursor. However, CAI and CAII remains constant in the range (0-1). It is due to a narrow porosity and a reduction of pore volume. The ratio  $P/P_0$  increased rapidly between 0 and 0.3, after this value it becomes constant.

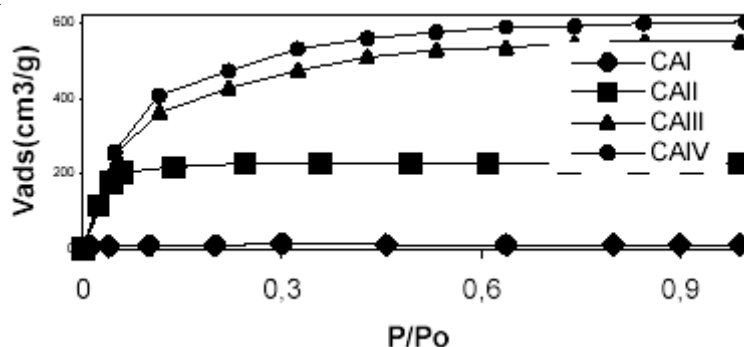


Fig. 1. N<sub>2</sub> adsorption isotherm of activated carbons CAI, CAII, CAIII and CAIV

The isotherms of nitrogen adsorption at 77 K for the CAI, CAII, CAIII and CAIV activated carbons can be attributed to type I according to the IUPAC classification with replenishment of the micropores at low relative pressures, characteristic of the microporous materials. The adsorption isotherms are employed to deduce the BET surface area ( $S_{BET}$ ), total pore volume ( $V_T$ ) and average pore diameter ( $D_p$ ), the results are shown in Table-2.

TABLE-2  
SURFACE AREA OF AND OTHER CHARACTERISTICS OF  
ACTIVATED CARBONS CAI, CAII, CAIII AND CAIV

Samples	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{T}}$ (cm <sup>3</sup> /g)	$D_p = 4V_{\text{T}}/S_{\text{BET}}$ (nm)
CAI	35	0.015	1.71
CAII	737	0.380	1.99
CAIII	1184	0.560	1.92
CAIV	1277	0.608	1.96

The area surface and total pore volume increasing in function of the degree of activation in the following order: CAI < CAII < CAIII < CAIV.

### Sorption studies

**Effect of the contact time on the adsorption:** Figs. 2(a,b) represent the adsorbed quantities of the phenolic compounds by the activated carbon precursors according to the time of adsorption kinetics study. The adsorption of phenol by the precursors is maximal at 1.5 h and *p*-cresol is maximal at 2 h. The equilibrium of adsorption was established more quickly for phenol than *p*-cresol for all precursors.

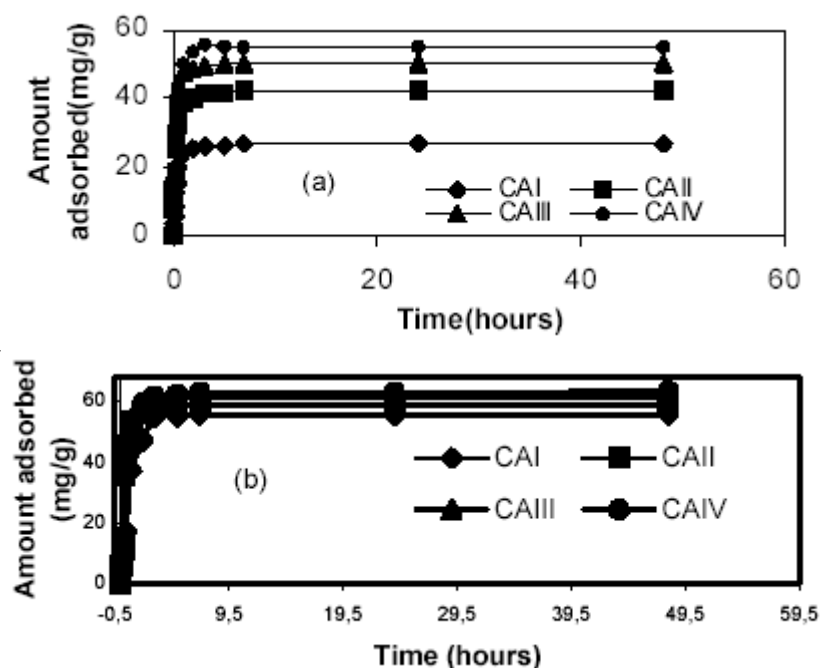


Fig. 2. Effect of contact time of adsorption of phenol (a) and *p*-cresol (b) by activated carbons, CAI, CAII, CAIII and CAIV at 25°C and adsorbate concentration of 75 mg/L

**Effect of initial concentrations on the adsorption:** The isotherms for the adsorption of phenol and *p*-cresol on activated carbons developed from lignocellulosic materials are shown in Figs. 3(a-b) at 25°C. The adsorption is positive and regular. The amount adsorbed of phenolic compounds increases with increase of the concentration and also with increase of the area surface for all prepared activated carbons. The uptake by CAIV is 75 % for phenol and 90 % for *p*-cresol, respectively.

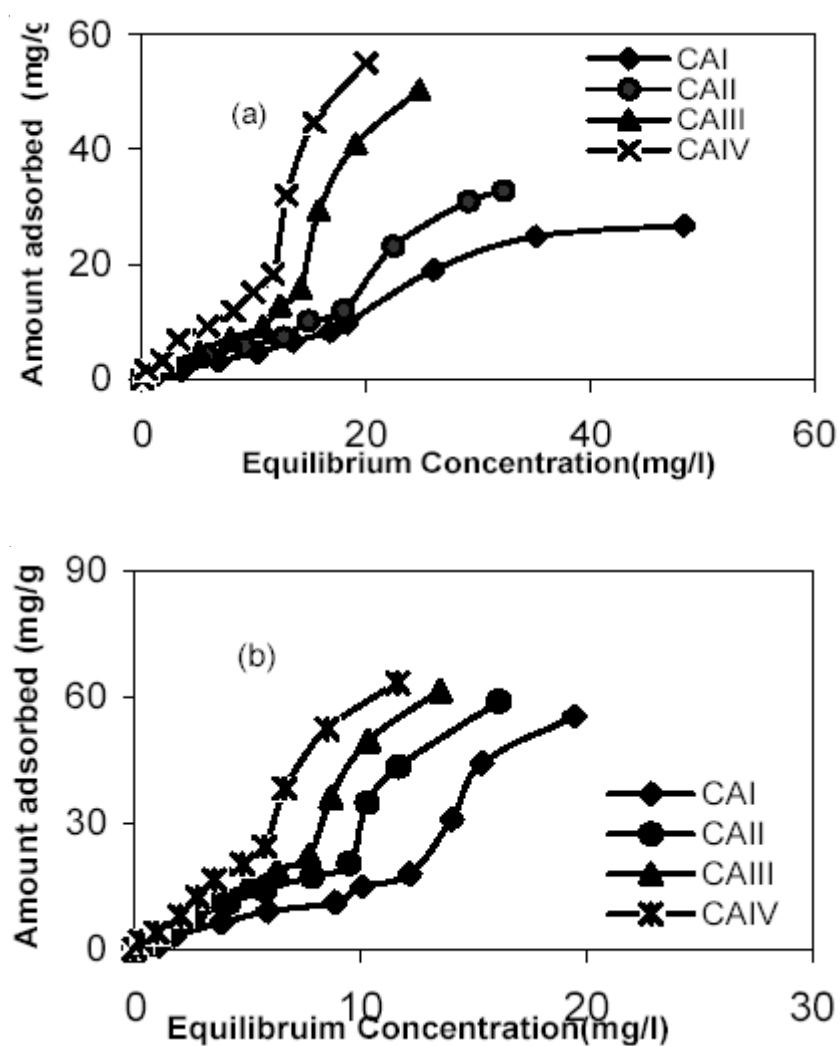


Fig. 3. Adsorption of phenol (a) and *p*-cresol (b) on activated carbons, CAI, CAII, CAIII and CAIV at 25°C

The equilibrium of a solute separated between liquid and solid phase is described by the Langmuir model, which suggests a monolayer adsorption, with no lateral interaction between the adsorbed molecules. This model is expressed by the following equation:

$$\frac{1}{Q_e} = \frac{1}{Q_0 \cdot b \cdot C_e} + \frac{1}{C_e} \quad (2)$$

where  $C_e$  is the concentration of phenolic solution ( $\text{mg L}^{-1}$ ) at equilibrium. The constant  $Q_0$  gives the theoretical monolayer adsorption ( $\text{mg L}^{-1}$ ) and  $b$  is related to the energy of adsorption ( $\text{L mg}^{-1}$ ). A plot of  $1/Q_e$  vs.  $1/C_e$  is linear Figs. 4 (a) for phenol and 4(b) for *p*-cresol, the monolayer adsorption capacity. Tables 2 and 3 give the values of  $Q_0$  and  $b$  for every type of precursor prepared.  $Q_0$  was found to be  $476 \text{ mg g}^{-1}$  and  $b$ ,  $0.017 \text{ l mg}^{-1}$  for phenol,  $476.2 \text{ mg g}^{-1}$  and  $b$ ,  $0.011 \text{ L mg}^{-1}$  for *p*-cresol with CAIV like adsorbent. The essential characteristics of the Langmuir isotherm, can be expressed by a dimension less constants, called equilibrium parameter  $R_L$ <sup>12</sup>.

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (3)$$

where  $b$  is the langmuir constant and  $C_0$  is the initial concentration ( $\text{mg/g}$ ),  $R_L$  values indicate the type of isotherm. The  $R_L$  values between 0 and 1 indicate favourable adsorption. The  $R_L$  values were found to be between 0 and 1. With CAIV adsorbent and  $75 \text{ mg/L}$  of concentration for all adsorbats,  $R_L$  is 0.432 for phenol and 0.543 for *p*-cresol.

TABLE-3  
LANGMUIR ISOTHERM CONSTANTS FOR THE ADSORPTION OF  
PHENOL (a) AND ADSORBATE CONCENTRATION OF  $75 \text{ mg/L}$

Langmuir constants	Phenol			
	CAI	CAII	CAIII	CAIV
$Q_0$ (mg/L)	34.010	90.900	120.500	476.000
$b \cdot 10^2$ (L/g)	1.730	0.750	0.920	1.760
$R^2$	0.978	0.979	0.974	0.975

TABLE-4  
LANGMUIR ISOTHERM CONSTANTS FOR THE ADSORPTION OF  
*p*-CRESOL BY ACTIVATED CARBONS CAI, CAII, CAIII AND CAIV  
AND ADSORBATE CONCENTRATION OF  $75 \text{ mg/L}$

Langmuir constants	<i>p</i> -Cresol			
	CAI	CAII	CAIII	CAIV
$Q_0$ (mg/L)	126.000	208.330	312.500	476.200
$b \cdot 10^2$ (L/g)	1.420	1.440	1.200	1.120
$R^2$	0.979	0.998	0.947	0.989

**Effect of temperature:** The amount adsorbed of phenol and *p*-cresol at different temperature into activated carbons for 75 mg/L of concentration is shown in Fig. 4(a-b). Small change in temperature decreased the amount adsorbed of phenolic compounds. Adsorption values of differential heat,  $\Delta H$ , were calculated from the maximal capacity of adsorption at two different temperatures, using the eqn. 4 of Vant' Hoff.

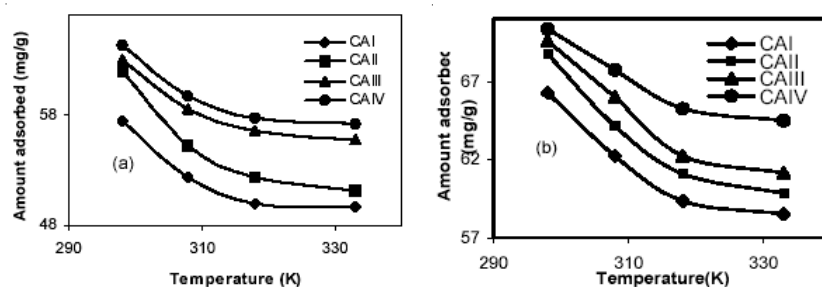


Fig. 4. Effect of temperature of adsorption of phenol (a) and *p*-cresol (b) by activated carbons, CAI, CAII, CAIII and CAIV for 10 h and adsorbate concentration of 75 mg/L

$$\ln \frac{Q_2}{Q_1} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

where, R is the perfect gas constant,  $Q_1$ ,  $Q_2$  are the adsorbed quantities at the equilibrium (mg/g),  $T_1$ ,  $T_2$  the temperatures (K) in a relatively near temperature domain. The results are shown in Fig. 5(a-b) and Table-5. The negative values of  $\Delta H$  confirm the exothermic nature and the decreased randomness at the solid/solution interface during the adsorption of phenolic compounds. The adsorption is advantageous to low temperature.

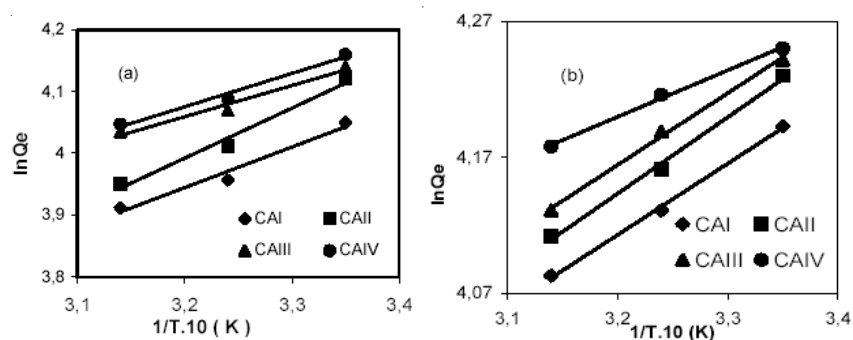


Fig. 5. Van toff plots for the adsorption of phenol (a) and *p*-cresol (b) by activated carbons CAI, CAII, CAIII and CAIV for 10 h and adsorbate concentration of 75 mg/L



TABLE-5  
DIFFERENTIAL HEATS OF THE ADSORPTION, FOR THE  
ACTIVATED CARBONS CAI, CAII, CAIII AND CAIV FOR 10 h AND  
ADSORBATE CONCENTRATION OF 75 mg/L

Compound	$\Delta H$ (KJ/mol)			
	CAI	CAII	CAIII	CAIV
Phenol	-5.484	-6.747	-4.171	-4.485
<i>p</i> -Cresol	-4.354	-4.677	-4.385	-2.842

**Effect of pH:** The effect of pH of the solution on the adsorption capacity of activated carbons CAI, CAII, CAIII and CAIV for substituted phenols is shown in Figs. 6(a-b). At low pH, the amount of phenols adsorbed increases slightly with the pH and at certain value of pH, there is a decrease in the value of  $Q_e$  while pH increases.

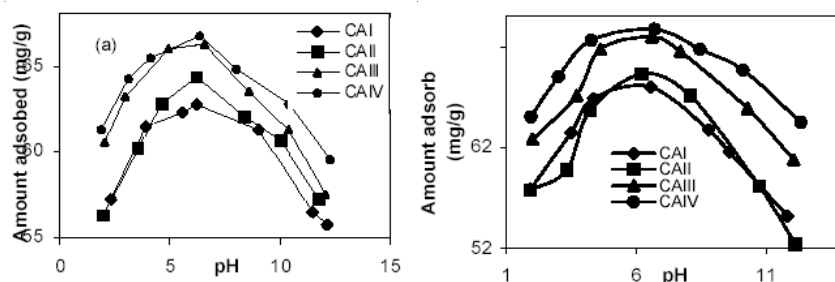


Fig. 6. Effect of pH on the adsorption of phenol (a) and *p*-cresol (b) by activated carbons, CAI, CAII, CAIII and CAIV for 48 h, and adsorbate concentration of 75 mg/L

The results indicate that the phenolic compounds are preferentially adsorbed on surface of the activated carbons in molecular form. At low pH values, they are not dissociated. The activated carbons used continue progressively acquiring negative charge from the external to the internal surface of the pores as the solution pH increases from 4.3 to 12.4 for CAIV activated carbon, the amount of phenolic compound adsorbed depends also on the surface charge<sup>6</sup>.

### Conclusion

The results show that the preparation of the carbon materials to remarkable adsorbing power can be obtained from jujube shells in presence of a chemical agent, using chemical activation or combined activation (chemical and physical activation with CO<sub>2</sub>). Important specific surfaces were obtained (1184 and 1277 m<sup>2</sup>/g) by the adsorption of nitrogen at 77 K.

the activating agent, has an important role in the development of the of these materials and puts in evidence that: (a)  $ZnCl_2$  gives the activated carbons having some porous parameters, especially micropores more than the quantity in salt and also by combined activation (chemical activation followed by physical activation with the  $CO_2$ ). (b) 74 % of the phenol in solution, 90 % of the *p*-cresol were removed by the activated carbon CAIV prepared by combined activation. The removal of phenolic substances follows the order  $CAI < CAII < CAIII < CAIV$ . (c) The values obtained of the differential heats for our samples ( $\Delta H < 10$  KJ/mol) confirm that the interactions with the phenol and the *p*-cresol are physical nature. (d) Neutral pH was favoured the adsorption of the phenolic compounds by activated carbons. So, the adsorption capacities of the activated carbon for the phenols depended on the degree of activation of the activated carbon, the solubility of the phenol compound in water and the hydrophobicity of substituents of the phenols. Thus, the adsorption capacity across with increased development of carbon surface area and porosity, with decreased water solubility of phenols compound and with increased hydrophobicity of its substituents<sup>12</sup>.

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