

# Effect of oxidant treatment of date pit activated carbons application to the treatment of waters

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## Abstract

Three activated carbons have been prepared from dates stones, by carbonization without adjuvant and by chemical activation with  $ZnCl_2$  and KOH.

According to the nature of the adjuvant, the activated carbons present different porosities. Chemical activation of the date stones with KOH produces an activated carbon having mésoporosity as well developed as in the  $ZnCl_2$  activation. This last process led also to develop the microporosity more than KOH activation.

The surface area, pore texture, and dosage of Boehm, of the activated carbons have been studied.

Adsorption at 298 K of phenol, *p*-cresol and *o*-chlorophenol from aqueous solutions on activated carbons has been studied. The adsorption capacity of the activated carbons depended on the surface area and porosity of the carbon, the solubility of the phenolic compounds, and the hydrophobicity of the substituent.

The modification of the porous texture and the chemical nature of the surface of activated carbons have been realized by oxidation with nitric acid. This oxidation lead to a considerable decrease of the surface area  $S_{N_2}$  and of the microporeux volume  $W_0$ , fixing a large amount of oxygen surface groups who influences negatively to the properties of adsorption of the activated carbons.

A heat treatment of these activated carbons leads to a reduction of the concentration of the oxygen groups and therefore an amelioration of the adsorption capacity.

*Keywords:* Substituted phenols adsorption; Activated carbons; Date stones; Acid treatments; Thermal treatment

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## 1. Introduction

Carbon adsorbents prepared from different precursors are widely used for concentration,

pre-treatment, and separation of organic substances present in air, soil, and water [1]. Fruit stones are appropriate raw material for the production of activated carbons [2–5]. The use of these materials as adsorbents of inorganic and organic pollutants from water is due to their unique

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versatility resulting from their high surface area, porous structure, high adsorption capacity, and surface chemical nature, which can be appropriately modified by physical and chemical treatments to enhance the extent of a given adsorption process [6].

Both the nature of the precursors and the method of activation have a strong influence on the porous structure and adsorption properties of the resulting activated carbons.

Various methods of activation have been used to obtain activated carbons from agricultural waste products. The so-called chemical activation refers to the carbonization of the precursor after addition of substances that restrict the formation of tar ( $\text{H}_3\text{PO}_4$ ,  $\text{ZnCl}_2$ ,  $\text{KOH}$ , etc.); in this way, a carbonized product with a well-developed porosity (after appropriate washing) may be obtained in a single operation. The chemical incorporated to the interior of the precursor particle reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinking of the particle; in this way, the conversion of the precursor to carbon is high, and once the chemical is eliminated after the heat treatment, a large amount of porosity is formed [7].

Chemical characteristics of the carbon surface have peculiar effects on its adsorptive properties and these surface properties can be modified by rising the number of surface oxygen-containing groups. Indeed, different treatments with oxidizing agents are able to create functionalized groups on external and porous surface of the material increasing the hydrophilic character at the same time. Several routes can be considered to achieve this surface functionalization of activated carbon especially in liquid phase, by treatment with  $\text{HNO}_3$  or  $\text{H}_2\text{O}_2$ .

In the present study we have investigated the influence of both the porous texture and the chemical nature of a series of activated carbons prepared from date pits on the adsorption process of phenolic compounds, such as: phenol,

*p*-cresol, *o*-cresol and *o*-chlorophenol from aqueous solutions at 298 K under static conditions.

## 2. Experimental

### 2.1. Preparation of activated carbons

Activated carbons used in this study were prepared from date pits. Date pits were crushed and sieved to a particle size of 0.5–1 mm in diameter. The precursor is impregnated with chemical reagent in a solid form. The impregnated precursor was carbonized in horizontal furnace under a flow (90 mL/min) of  $\text{N}_2$  with a heat low of 5 K/min until the final temperature of the pyrolyse. After cooling in  $\text{N}_2$ , the carbons were thoroughly treated by a diluted solution with chloride acid under reflux ebullition for three hours in order to extract the alkalic compound formed and reagent excess. The charcoals are recuperated after filtering and over washing with distillate boiling water until the test on the filtrate on silver nitrate is negative. Then they are dried in oven.

Activated carbons will be referred to in the text as DC (these samples were pyrolyzed at 873 K with a heat low of 5 K/min), DK, (these samples were impregnated with 9 mmol of  $\text{KOH}$  and then pyrolyzed at 1073 K with a heat low of 5 k/min), DZ, (these samples were impregnated with 3.52 mmol of  $\text{ZnCl}_2$  and pyrolyzed at 873 K with a heat low of 5 K/min).

In order to form carbon–oxygen complexes on the surface of some of those activated carbons, these carbons were treated with nitric acid according to the following procedure: 10 cm<sup>3</sup> of concentrated nitric acid were added to 1 g of activated carbon (samples DK and DZ); after heating at 353 K to dryness, the carbons were washed with distilled water and heated in an oven at 383 K overnight. The samples so obtained will be referred in the text as DKN and DZN respectively.

The activated carbons obtained DKN and DZN are heated thermally under a flow of  $\text{N}_2$

Table 1

Textural characteristics of the activated carbon samples from date pits

Sample	$S_{N_2}$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{CO_2}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{DR}$ (CO <sub>2</sub> ) (cm <sup>3</sup> g <sup>-1</sup> )	$V_{meso}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{macro}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_t$ (cm <sup>3</sup> g <sup>-1</sup> )	pH
DC	640	1167	0.45	0.08	0.12	0.65	6.8
DZ	882	1509	0.59	0.09	0.38	1.06	7.4
DK	1032	1450	0.56	0.31	0.34	1.21	10.2

with a heat low of 5 K/min until the final temperature of treatment and maintained during 1 h to this temperature.

## 2.2. Characterization of activated carbons

### 2.2.1. Textural characterization

Some of the textural characteristics of activated carbons are compiled in Table 1, which shows values for:  $S_{N_2}$ , the nitrogen surface area, obtained by applying the BET method to the N<sub>2</sub> adsorption isotherms at 77 K;  $S_{CO_2}$ , obtained by applying the Dubinin Radushkevich (DR) equation to the CO<sub>2</sub> adsorption isotherms at 273 K;  $V_2$  and  $V_3$ , the pore volumes contained in pores with diameters within 3.7 and 50 nm, and higher than 50 nm, respectively, obtained from mercury porosimetry.

### 2.2.2. Chemical characterization

To measure the pH values of the aqueous suspensions of the carbon samples, 1-g portions of carbons were mixed with 20 cm<sup>3</sup> of CO<sub>2</sub> free distilled water; the suspensions were shaken mechanically for 48 h at 298 K and then their pH values were determined using a glass electrode. The values obtained are shown in Table 1. The acidic function group, such as carboxylic, lactonic and phenolic was determined, following the method proposed by Boehm [8,9]. We have attempted to differentiate these acidic groups, in the sample DK, DZ and DC by neutralization with bases of different basicities: NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and NaOH. According to Boehm, NaHCO<sub>3</sub>

neutralizes carboxylic groups, Na<sub>2</sub>CO<sub>3</sub> neutralizes carboxylic and lactonic groups and NaOH neutralizes carboxylic, lactonic and phenolic groups, so NaOH gives a measure of the total surface acidity of carbons. The results obtained are summarized in Table 5.

### 2.2.3. Adsorption of phenolic compounds under static conditions

The adsorption processes from aqueous solutions of the different phenolic compounds, phenol, *p*-cresol, *o*-cresol and *o*-chlorophenol, on the activated carbons were carried out at 298 K.

For this purpose, aqueous solutions with different initial known concentrations were used. Adsorption isotherms were determined by using stoppered flasks containing 0.1 g of carbon/100 cm<sup>3</sup> of solution. They were kept in a thermostat shaker bath at 298 K for 5 days, after which the equilibrium concentrations was determined spectrophotometrically at the maximum absorbance wavelength ( $\lambda$ ) shown in Table 2, using a Jasco V-530, spectrophotometer. Table 2 also

Table 2

Physical characteristics of phenolic compounds

Phenol compound	$\lambda$ (nm)	pK <sub>a</sub> at 298	Solubility at 298 K, g/100 g H <sub>2</sub> O
Phenol	269	9.96	9.3
<i>p</i> -Cresol	276	10.17	2.3
<i>o</i> -Chlorophenol	273	8.80	2.6

shows some physical characteristics of the phenolic compounds used.

### 3. Results and discussion

#### 3.1. Activated carbons characterization

Table 1 reports the characterization of the porous structure of the activated carbons. The DC char shows an interesting BET surface area for use as a precursor for activated carbon through further activation.

The main factor affecting the surface area and the micropore size distribution is the nature of chemical reagent introduced in the precursor during impregnation. Chemical activation of the date pits with  $\text{ZnCl}_2$  produces an activated carbon having microporeux volume more important ( $0.59 \text{ cm}^3/\text{g}$ ) than that activated carbon DC whose volume is the order of  $0.45 \text{ cm}^3/\text{g}$ . Similar results have been found by other authors [10] that the chemical activation of date pits by different activating agents ( $\text{ZnCl}_2$  and  $\text{H}_3\text{PO}_4$ ) produced activated carbons of nature microporeuse.

We also note that potassium hydroxide activation produced activated carbons with more important mésoporeux volume than the one impregnated by  $\text{ZnCl}_2$ . The development of the porosity of date pits by chemical activation with  $\text{ZnCl}_2$  or KOH is taken in detail in a previous paper [11,12].

Thus, widening of the micropore size together with the development of meso- and macroporosity are important features as regards the potential use of these activated carbons as adsorbents for liquid phase applications such as water and waster treatment. The apparent surface areas compare well with those of many commercial activated carbons used in these applications [13,14].

#### 3.2. Adsorption of phenolic compounds

Adsorption isotherms of *o*-chlorophenol, *p*-cresol and phenol on activated carbons DK, DZ, and DC are depicted in Fig. 1.

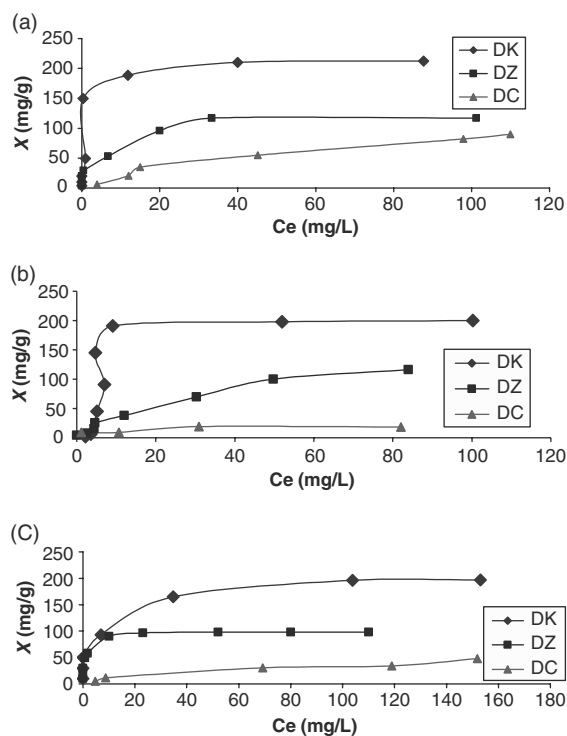


Fig. 1. Adsorption isotherms of (a) phenol (b) *p*-cresol, (c) *o*-chlorophenol at 298 K on activated carbons.

The adsorption isotherm plots present an L-shape, according to the Giles classification [15]; competition between phenols and water molecules for active sites on carbons is therefore weak and were very well fitted by the Langmuir equation, from which the adsorption capacity,  $X_m$ , and the constant,  $B$ , were calculated. These parameters, and the relative affinities,  $BX_m$  of the phenols toward the surface of the adsorbents are compiled in Table 3 [16].

High correlation was found between  $X_m$  and BET areas; the value of  $X_m$  for the different phenols increases with the surface area and porosity of the activated carbons. Thus, activated carbon DK with the highest surface area and the most developed porosity has the highest adsorption capacity for all phenols.

The adsorption capacity of a given activated carbon for the different phenols is, in general,

Table 3

Results obtained from the Langmuir equation applied to the adsorption isotherms of phenolic compounds on activated carbons

Sample	Phénols	$X_m$ (mg g <sup>-1</sup> )	B (L mg <sup>-1</sup> )	$BX_m$ (L g <sup>-1</sup> )
DC	Phénol	54.94	0.02	1.3
	<i>p</i> -Crésol	58.14	0.02	1.2
	<i>o</i> -Chlorophénol	57.80	0.03	1.7
DZ	Phénol	103.09	0.16	16.5
	<i>p</i> -Crésol	188.68	0.02	3.8
	<i>o</i> -Chlorophénol	120.50	0.75	90.4
DK	Phénol	169.49	1.21	205.1
	<i>p</i> -Crésol	322.58	0.34	109.7
	<i>o</i> -Chlorophénol	208.33	1.67	347.9

related to their solubility in water [17] and to the hydrophobic character of their substituents [18]. Thus, *p*-cresol, possessing very low water solubility, is in, general adsorbed on the activated carbons to a greater extent than the other phenols.

However, *p*-cresol and *o*-chlorophenol which have a hydrophobic group are also adsorbed to a greater extent than phenol [19].

The relative affinity,  $BX_m$ , of the phenols toward the surface of the adsorbents increases with the degree of activation of the activated carbon (from DC to DK), in accordance with their higher adsorption rate and porous structure.

As is well known [19,20], the adsorption of phenolic compounds on activated carbon implies the formation of electron donor-acceptor complexes in which the basic surface oxygen groups act as donors and the aromatic ring of the adsorbate as acceptor.

Thus, Coughlin and Ezra [21] also suggested that phenol adsorption on carbons involves dispersive forces between the  $\pi$ -electrons in phenol and the  $\pi$ -electrons in carbons.

For a given activated carbon and for the different phenolic compounds studied, the value of  $BX_m$  increases in the following order:

$BX_m$  (*p*-cresol) <  $BX_m$  (phenol) <  $BX_m$  (*o*-chlorophenol).

This order has been observed previously for other activated carbons [19].

This phenomenon is explained by the effect of the electron withdrawing or electron donating properties of the substituents of the phenol compound.

The electron withdrawing groups of the Cl in the *o*-chlorophenol encourages the formation of the complex donor-acceptor better than the CH<sub>3</sub> group in the *p*-cresol how has electron-donating properties.

### 3.3. Modifications of the porous texture and the chemical nature of the surface of an activated carbon by oxidization to the nitric acid

The oxidization of the activated carbon DK and DZ With nitric acid to produce sample DKN and DZN bring a large decrease in both the surface specific  $S_{N_2}$  and in the volume  $V_{DR}(CO_2$  microporeux), as shown by the Table 4. The same result has been observed previously for other activated carbons from lignocellulosiques materials treated with HNO<sub>3</sub> [22].

The majority of the authors assigns the reduction of the surface specific  $S_{N_2}$  and the volume  $V_{DR}(CO_2$  microporeux) to the destruction of the micropores during the violent oxidization to the nitric acid. Similar results have been found

Table 4  
Textural characteristics of modified activated carbons

Carbon	$A_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{DR}} \text{CO}_2$ (cm <sup>3</sup> /g)	$V_{\text{més}} \text{o}$ (cm <sup>3</sup> /g)	$V_{\text{macro}}$ (cm <sup>3</sup> /g)
DK	1040	0.40	0.34	0.27
DKN	789	0.30	0.30	0.32
DKN400	980	0.28	0.32	0.31
DKN600	1010	0.27	0.38	0.30
DKN800	1030	0.25	0.36	0.30
DZ	850	0.59	0.09	0.38
DZN	520	0.45	0.08	0.44
DZN400	670	0.40	0.12	0.42
DZN600	830	0.38	0.20	0.41
DZN800	845	0.35	0.18	0.40

by other authors [23], showed that more the degree of activation of the initial sample is important more the reduction of  $S_{\text{N}_2}$  and the  $V_{\text{DRCO}_2}$  after treatment to the nitric acid is big. Indeed, an elevated degree of activation of the samples returns the partitions of the pores thin and easy to destroy by oxidization to the nitric acid.

The Table 4 also show that the oxidization in the nitric acid of activated carbon DK and DZ to give activated carbon DKN and DZN respectively, leads to a weak reduction of the volume mésoporeux and a slight increase of the volume macroporeux.

The oxidization is followed here by a heat treatment; the results are consigned in the Table 4. These heat treatments were carried out to partially

remove the oxygen surface complexes from activated carbon in an attempt to further elucidate their chemical nature and thermal stability.

The surface area value increases with heat treatment, reaching for sample treated at 1073 K a similar value to that of the original sample. However, the micropore volume decreases with the heat treatment which, at the same time, produces a widening of the microporosity.

The mesopore volume, increase with the heat treatment, however, the macropore volume does not affect.

Table 5 summarizes the surface global acidity according to Boehm titration. Results are directly compared to those related to the corresponding non-oxidized solids.

Table 5  
Acid properties of oxidized and non-oxidized activated carbons

Activated carbon	NaOH (meq g <sup>-1</sup> )	Na <sub>2</sub> CO <sub>3</sub> (meq g <sup>-1</sup> )	NaHCO <sub>3</sub> (meq g <sup>-1</sup> )
DK	0.69	0.46	0.32
DKN	2.03	1.50	0.95
DKN400	1.60	1.05	0.62
DKN600	0.88	0.66	0.40
DKN800	0.57	0.43	0.23
DZ	1.22	0.80	0.48
DZN	2.72	2.17	1.22
DZN400	1.90	1.30	0.80

Table 6  
Elementary chemical analyses of the different activated carbons

Carbon (%)	DZ	DZN	DZN800	DK	DKN	DKN800
C	82.79	60.3	75.94	75.04	61.64	74.23
H	1.13	1.58	0.53	0.46	1.19	0.35
O	4.62	22.3	5.78	9.46	18.3	3.28
N	1.57	2.51	2.74	0.43	0.46	0.65

The oxidation of activated carbons DK and DZ by  $\text{HNO}_3$  create a very important number of acidic functions phénolique, lactones and carboxylique. The thermal treatment of these two activated carbons oxidized previously in the nitric acid leads to the reduction of the concentration of these three oxygenated groups; it is to note that more the temperature of treatment increases, more the content of the acidic functions decreases and reaches with DKN800 coals and DZN800 of the values lower to those gotten for activated carbons DK and DZ before oxidization.

There is a close relation between the acidity of activated carbons and their atomic oxygen concentration as it can be seen in Tables 5 and 6. It displays that the increase of surface oxygen concentration directly raises the amount of acidic groups in every case.

Activated carbons DKN and DZN shine by important contents in oxygen and in hydrogen, revealing the presence of many groups of surface containing these elements as phénoliques, carboxyliques and lactones functions. When the activated carbons DKN and DZN were heated at  $800^\circ\text{C}$ , the two activated carbons adopt a similar behaviour;

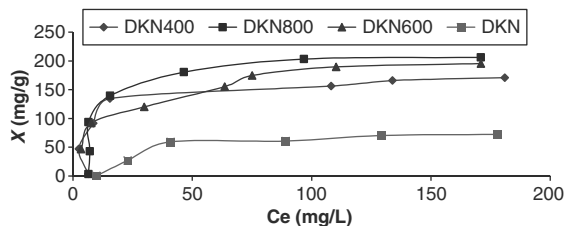


Fig. 2. Adsorption isotherms of phenol.

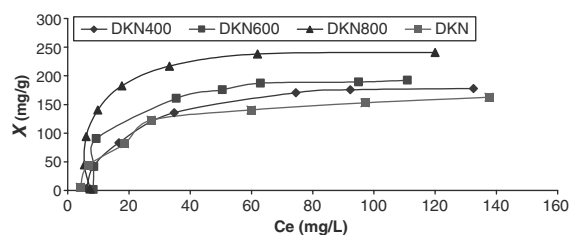


Fig. 3. Adsorption isotherms of *o*-cresol.

a strong reduction of the tenure in oxygen and in hydrogen. Indeed him (%) in oxygen decreases 22.3% for DZN to 5.78% for DZN800 and 18.3% for the DKN to 3.28% for the DKN800.

#### 3.4. Adsorption of the phenol and *o*-cresol on surface modified of the activated carbons

Adsorption isotherms of phenol and *o*-cresol on activated carbons from series DZ and DK are depicted respectively in Figs. 2–5.

Table 7 shows that the capacity of adsorption of the DK and DZ is decreased strongly after oxidization with nitric acid.

Some similar results have been found by other authors [24] assigns the reduction of the adsorption

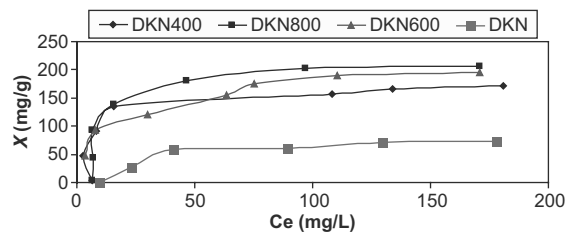


Fig. 4. Adsorption isotherms of phenol.

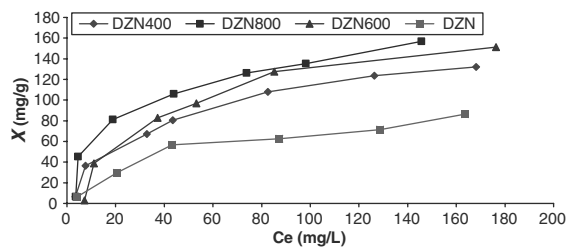


Fig. 5. Adsorption isotherms of *o*-cresol.

of the phenolic compounds with the oxidization of the surface of activated carbons; however without providing a quantitative explanation however. In other words, the increase of the activated carbons oxidized affinity opposite to water entails a reduction of the surface accessible to the phenolic compounds.

The Table 7 also shows that the capacity of adsorption of the phenol and *o*-cresol increases with the heat treatment temperature, in other words when the number of oxygenated functions implanted to the surface of the activated carbons decreases. These results can be interpreted by a fixing of the phenol and *o*-cresol on basic sites of the surface of the activated carbons. Indeed the oxygenated functions implanted to the surface of the activated carbons during the oxidization with nitric acid, conceal a part of these sites which becomes inaccessible to the molecules of the phenol and *o*-cresol. Increase the temperature of heat treatment, the concentration of these oxygenated groups decreases and the capacity of adsorption of activated carbons increases.

Table 7

Results obtained from the Langmuir equation applied to the adsorption isotherms of phenolic compounds on oxidized and non-oxidized activated carbons

Carbon actif	Phénols	$X_m$ (mg g <sup>-1</sup> )	B (L mg <sup>-1</sup> )	$BX_m$ (L g <sup>-1</sup> )
DZ	Phénol	103.09	0.16	16.5
	<i>o</i> -crésol	181.81	0.05	9.1
DZN	Phénol	70.69	0.04	2.8
	<i>o</i> -crésol	123.84	0.02	2.5
DZN400	Phénol	100.62	0.06	6
	<i>o</i> -crésol	163.30	0.03	4.8
DZN600	Phénol	138.88	1.12	155.5
	<i>o</i> -crésol	191.51	0.75	143.6
DZN800	Phénol	139.04	1.20	166.8
	<i>o</i> -crésol	196.84	0.8	157.8
DK	Phénol	169.49	1.21	205.1
	<i>o</i> -crésol	238.10	0.37	88.1
DKN	Phénol	99.01	0.05	4.9
	<i>o</i> -crésol	131.58	0.02	2.6
DKN400	Phénol	158.86	0.13	20.7
	<i>o</i> -crésol	193.83	0.03	5.8
DKN600	Phénol	181.81	0.95	172.7
	<i>o</i> -crésol	288.67	0.43	124.1
DKN800	Phénol	196	1.65	323.4
	<i>o</i> -crésol	303	0.85	257.5

#### 4. Conclusion

Date pits have a high potential as starting for activated carbons showing good performances as adsorbent for the depollution of waters containing phenolic compounds.

The characteristics of the activated carbons obtained depend on the activation process and the nature of the chemical reagent.

Chemical activation of the date pits with  $ZnCl_2$  or KOH produces an activated carbon have a high specific surface area reaching about 880 and 1030  $m^2/g$  for DZ and DK carbon, respectively.

The adsorption capacities of the activated carbon for the phenols studied depended on the degree of activation of the activated carbon, the solubility of the phenol compound in water, and the hydrophobicity of the substituents of the phenols. Thus, the adsorption capacity rose with increased development of carbon surface area and porosity, with decreased water solubility of the phenolic compound, and with increased hydrophobicity of its substituent.

The relative affinity of the phenolic compounds toward the surface of the activated carbon was related to the electron donor-acceptor complexes formed between the basic sites on the carbon surface (basic surface oxygen complexes and/or  $\pi$  electron-rich regions at the basal planes) and the aromatic ring of the phenols. Thus, the relative affinity increases with the basicity of the carbon surface and with the electron-withdrawing property of the substituent of the phenol.

The oxidization of activated carbons DK and DZ with nitric acid provoked a considerable increase of the acidic functions (carboxylique, lactonique and phenolique) and decreased the capacity of adsorption of the phenolic compounds. The functions oxygenated of surface, implanted during oxidization with nitric acidic cover a part of the pores which becomes inaccessible to the molecules of the phenol and the *o*-cresol. The heat treatment to different temperatures under nitrogen of the oxidized activated carbons (DKN

and DZN) decreased strongly the acidic functions and increased the capacity of adsorption of the activated carbons. Indeed, the thermal treatment decreased the content of the oxygenated functions that decreased the access of the molecules phenolic to the surface of activated carbons by their considerably sterique clutter.

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