

A Controlled Nitric Acid Oxidation of an Olive Stones-based Activated Carbon: Effect of Oxidation Time

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A granular activated carbon, derived from olive stones, was oxidized with nitric acid for different periods of time in order to create more oxygenated functional groups without deeply affecting its framework. The changes in porous texture and morphology of carbon during acid treatment were evaluated by scanning electron micrograph (SEM), as well as N₂ and CO₂ adsorption. The surface functional groups on carbon surface were confirmed by FTIR spectroscopy, multibasic titration method of Boehm, pH of the point of zero charge measurement (pH_{PZC}), and temperature programmed desorption (TPD-MS) technique. Batch adsorption experiments were conducted to study the effect of nitric acid oxidation on the removal of Pb²⁺ and 2-nitrophenol molecules from aqueous solution at 30°C. The results showed that the acidic character of the plain carbon was enhanced by the creation of carboxyl, lactone and phenol groups from the first two hours of oxidation. These created groups were located at the entrance of narrow micropores. The reduction in specific surface area was not very significant. Furthermore, the raw material showed excellent Pb²⁺ adsorption capacity (318 mg.g⁻¹), which was improved by acid treatment. However, the uptake of the phenolic compounds decreased as a result of formation of new oxygen functionalities.

Keywords: Olive stones; Activated carbon; Oxidation, Surface oxygen complexes; Adsorption

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INTRODUCTION

Activated carbons (ACs) can be produced from any materials that have high carbon content and low inorganics, including wood, coal, petroleum coke, and agricultural residues (Baily *et al.* 1999; Kaszlo *et al.* 2000; Toles *et al.* 1997). Thanks to their exceptionally large surface areas, their well-developed internal pore structure, as well as their surface reactivity attributed to the existence of a wide spectrum of oxygen containing groups, ACs are extensively used as catalyst, catalyst support and also as adsorbents to capture a variety of species such as organic substances, metal ions, and gas/vapor adsorbate from gas/liquid phase (Tseng *et al.* 2006; Zhu *et al.* 2000; Aksoylu *et al.* 2001).

Carbon-oxygen surface groups are by far the most important surface groups that influence the surface characteristics such as wettability, polarity, acidity, and physico-chemical properties such as catalytic, electrical, and chemical reactivity of these materials. In fact, the combined oxygen has been found to be the source of the property that renders carbon useful or effective in certain respects (Rodriguez-Reinoso 1998; Mikhalev and Oye 1996; Li *et al.* 2002).

To increase the concentration of surface oxygen groups, oxidation procedures on dry or wet phase have been successfully applied (Santiago *et al.* 2005; Canizares *et al.* 2006). Being a strong oxidant, nitric acid has been the most used (Moreno-Castilla *et al.* 1998; Haydar *et al.* 2003; Huang *et al.* 2009; El-Hendawy, 2003; Mourao *et al.* 2011), and the severity of nitric acid oxidation can be adjusted or controlled by a combination of oxidant concentration, oxidation time and oxidation temperature. Unfortunately, the creation of new oxygenated groups on the surface has often led to reduction of surface area as well as micropore volume. Therefore, an oxidation can be considered as suitable and efficient only when the treated carbon retains its porous texture.

The present work represents a continuation of a previous work in our laboratory (Soudani *et al.* 2013), in which we studied the effect of nitric acid concentration on the different properties of a Lab-made activated carbon. The nitric acid oxidation of a H₃PO₄-activated carbon, derived from olive stones, was controlled by changing the residence times (2-36 h) of the carbon on a 1 M nitric acid solution at boiling, in this work. The structural order and textural properties were followed by N₂ sorption at -196°C, CO₂ sorption at 0°C, and scanning electron micrographs (SEM). However, the chemical characteristics were performed by different techniques such as: Fourier Transform Infra Red spectroscopy (FTIR), Boehm titration method, pH of the point of zero charge (pH_{PZC}) measurements, and temperature-programmed desorption (TPD-MS) technique. Finally, the effect of this modification on the adsorption of a metallic molecule and an aromatic one were studied.

EXPERIMENTAL

Active Carbon Preparation

As a Mediterranean country, olive cultivation is particularly widespread throughout Tunisia. Therefore, olive stone is a very abundant agricultural by-product, and many results obtained made clear that this lignocellulosic precursor is a very adequate raw material to obtain active carbons (Lopez-Gonzales *et al.* 1980; Ubago-Pérez *et al.* 2006; Rios *et al.* 2006).

Olive stones were freed from the bagasse obtained as by-product in the olive oil industry, by washing with hot distilled water, to obtain grains sized to about 1 to 3 mm. Some amount of olive stones were impregnated with an aqueous solution of orthophosphoric acid (50%, w/w) at the weight ratio 1/3. The suspension of the olive stones in chemical impregnation solution was mixed at 110°C for 9 h. The impregnated material was dried and then carbonized in steam of nitrogen at 170°C for 30 min and finally at 410°C for 2 h 30 min. The resulting carbon, denoted as CAC, was then washed abundantly with distilled water until the elimination of all acid traces, and was dried overnight at 110°C. It was used in granular form, with a range size of 1 to 1.4 mm.

Nitric Acid Oxidation

About 30 g of CAC was mixed with 250 mL of 1 M nitric acid aqueous solution. The mixture was maintained under a reflux at boiling for 2, 4, 8, 16, and 36 hours. Subsequently, the resulting materials were filtered and extensively washed with distilled

water until the cleaning water pH was approximately 7. Finally, the samples were dried at 110°C. The samples so prepared were labeled CAC0, CAC2, CAC4, CAC8, CAC16, and CAC36 (zero refers to the virgin sample).

Porous Texture Characterization

The porosity of the activated carbons was deduced from the adsorption isotherms of N₂ at -196°C and CO₂ at 0°C. High resolution N₂ isotherms were carried out using an automatic gas sorption analyzer (ASAP 2020, Micromeritics). For these measurements, about 100 mg of samples were previously degassed at 250°C for 24 h. From N₂ adsorption isotherms, the apparent BET surface areas, S_{BET} , were obtained by applying BET equation. Total pore volumes, V_{T} , were obtained at $p/p^{\circ} = 0.95$ (Gurvitsch rule). The Dubinin-Radushkevich (DR) equation was applied to obtain the micropore volume, V_{mic} . Finally, the volumes of mesopore, V_{meso} , were deduced from the difference between V_{T} and V_{mic} . However, the application of DR equation to CO₂ adsorption isotherms leads to determination of the volume of narrow micropores, V_{CO_2} , of size lower than 0.7 nm (Garido *et al.* 1987).

The morphology of activated carbons was also analyzed employing a HITACHI S-3000N scanning electron microscope (SEM).

Chemical Surface Group's Characterization

The Boehm method (Boehm 1994) can be described as follows: 1 g of samples was placed during 72 hours, in 50 mL of 0.1 N solutions of: hydrochloric acid, sodium hydroxide, sodium carbonate, and sodium hydrocarbonate. Then, each solution was titrated with HCl or NaOH. The amount of acidic groups was determined on the assumption that NaOH neutralizes carboxyls, phenols, and lactone groups; Na₂CO₃ neutralizes carboxyls and lactone groups, and NaHCO₃ neutralizes only carboxyls. The basic groups content was obtained from the amount of HCl that reacted with the carbon.

The pH_{PZC} is the pH at the zero point of charge, which is the point at which the net charge of the adsorbent is zero. The pH_{PZC} of carbons was measured by the so-called pH drift method: aliquots with 50 cm³ of 0.01 M NaCl solutions were prepared in different flasks. Their pH values were adjusted to the value between 2 and 12 with the addition of 0.01 M solutions of HCl or NaOH. When, the pH value became constant, 0.15 g of activated carbon sample was added to each flask and it was shaken for 48 h. The final pH was measured after 48 h using pH meter Schott CG 825. The pH_{PZC} value is the point where the curve pH_{final} versus $\text{pH}_{\text{initial}}$ crosses the line $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$.

FTIR spectra were recorded on a Perkin Elmer 1310 spectrophotometer using the KBr disc method: samples of activated carbon were mixed with finely divided spectroscopic grade KBr in the ratio 1:400. Samples were dried for 24 h at 100°C. Background spectra of KBr and water vapor were subtracted. Spectra were recorded at a resolution of 4 cm⁻¹ using a minimum of 100 scans.

TPD followed by a mass spectrometer were performed by heating the samples up to 1000°C in helium flow of 50 mL/min, at a heating rate of 10°C/min. An omnistar quadrupole mass spectrometer from Balzers was used for evolving the amount of CO and CO₂.

Batch Adsorption Experiment

After studying the equilibrium time and the adequate pH, the adsorption of Pb^{2+} from the dilute aqueous solution was operated as follows: take a series of 100 mL glass flasks, containing 0.015 g of the powdered carbon and 50 mL solution of lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$) with an initial concentration of 0.1 g/L. The pH of the mixtures was maintained at 6, and shaken for 4 h at 30°C. The residual metal was estimated, in the filtered solution, using an atomic absorption spectrometer (GBC, Avanta Victoria Australia).

Adsorption isotherms of 2-nitrophenol (2NP) were determined by mixing 0.2 g of the powdered carbon with 200 mL of 2NP solutions of varying concentration. The mixtures were then shaken for 4 hours considered adequate to reach equilibrium, and at a temperature of 30°C. The residual phenolic compound was estimated, in the filtered solution, using a double beam UV-vis spectrophotometer (UV-1601, Shimadzu) at an absorbance of 353 nm.

The equilibrium adsorption amounts, q_e (mg/g) of Pb^{2+} and 2NP were calculated by,

$$q_e = ((c_0 - c_e)/m_{AC}) \times V \quad (1)$$

where c_0 (mg/L) is the initial concentration of solute, V (L) is the volume of solution, c_e (mg/L) is the equilibrium concentration, and m_{AC} (g) is the weight of AC.

Analysis of the adsorption isotherms of 2NP was performed by applying the linear Langmuir model equation (1918),

$$c_e/q_e = 1/(q_m + K_L) + c_e/q_m \quad (2)$$

where c_e and q_e are the amounts of substrate in solution and on the solid (adsorbent), and K_L is the Langmuir equation constant. The monolayer capacity, q_m , was estimated for both solutes from the respective slopes of the Langmuir plots.

RESULTS AND DISCUSSION**Porous Structure**

The nitrogen adsorption isotherms of virgin and oxidized samples are shown in Fig.1, and the different porous parameters are summarized in Table 1.

Table 1. Textural Parameters Obtained from the Adsorption of N_2 at -196°C and CO_2 at 0°C

Sample	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_T ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{mic} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{CO_2} ($\text{cm}^3 \cdot \text{g}^{-1}$)
CAC0	1000	0.459	0.446	0.013	0.409
CAC2	894	0.413	0.402	0.011	0.376
CAC4	925	0.423	0.416	0.007	0.379
CAC8	871	0.403	0.390	0.013	0.353
CAC16	871	0.405	0.392	0.013	0.288
CAC36	878	0.403	0.395	0.008	0.055

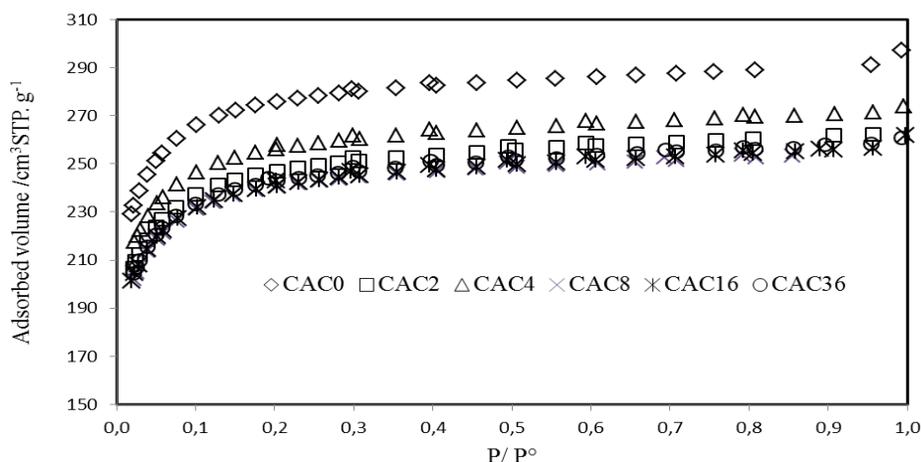


Fig. 1. N₂ adsorption isotherms at 77K for CAC and oxidized products

All the isotherms were of type I according to the Brunauer, Deming, Deming and Teller (BDDT) classification system (Brunauer 1943), which characterizes a microporous material. Furthermore, the high adsorption of N₂ at very low relative pressures values together with the little pronounced isotherm knee are indicative of the presence of narrow microporosity in the material (Gregg and Wsing 1982).

As expected, the treatment with nitric acid for different times decreases the nitrogen adsorption capacity of the samples, indicating thus minor modification in the pore volume and pore size. The textural data shown in Table 1 also imply that oxidation reduced the different porous parameters, except the volume of mesopore, which was almost constant within the experimental error. That means there was no destruction of micropore walls even after extended oxidation, and this reduction is related to the creation of new functional groups at the entrance of micropores. This fact can be deduced also from the observation of SEM images, shown in Fig. 2.

It can be clearly observed that the prepared carbon retained its porous structure and there was no widening of its porosity, even by extending the treatment (Fig.2 (c)). In contrast, controlling the oxidation by increasing acid concentration has often led to the destruction of carbon framework (Soudani *et al.* 2013; Khalifi *et al.* 2010; Ania *et al.* 2007).

On the other hand, the reduction had a more significant effect on the narrow microporosity determined from adsorption isotherms of CO₂ (V_{CO_2}). It seems that the access to this range of micropore was destroyed or hindered by the created new functional groups. Moreover, the evolution of V_{CO_2} against the oxidation time, plotted in Fig. 3, has shown a good linearity. This observation indicates that the basal plane was highly stable. Therefore, oxygen surface groups are located at the edges of the basal plane which are respectively weak sites of carbon structure and oxidation progresses slowly into the basal planes (Donnet and Bansal 1990). In addition, this linearity has potential to be very useful, especially if the modified carbons are to be used for the adsorption of some molecules, where the microporosity is also a key factor.

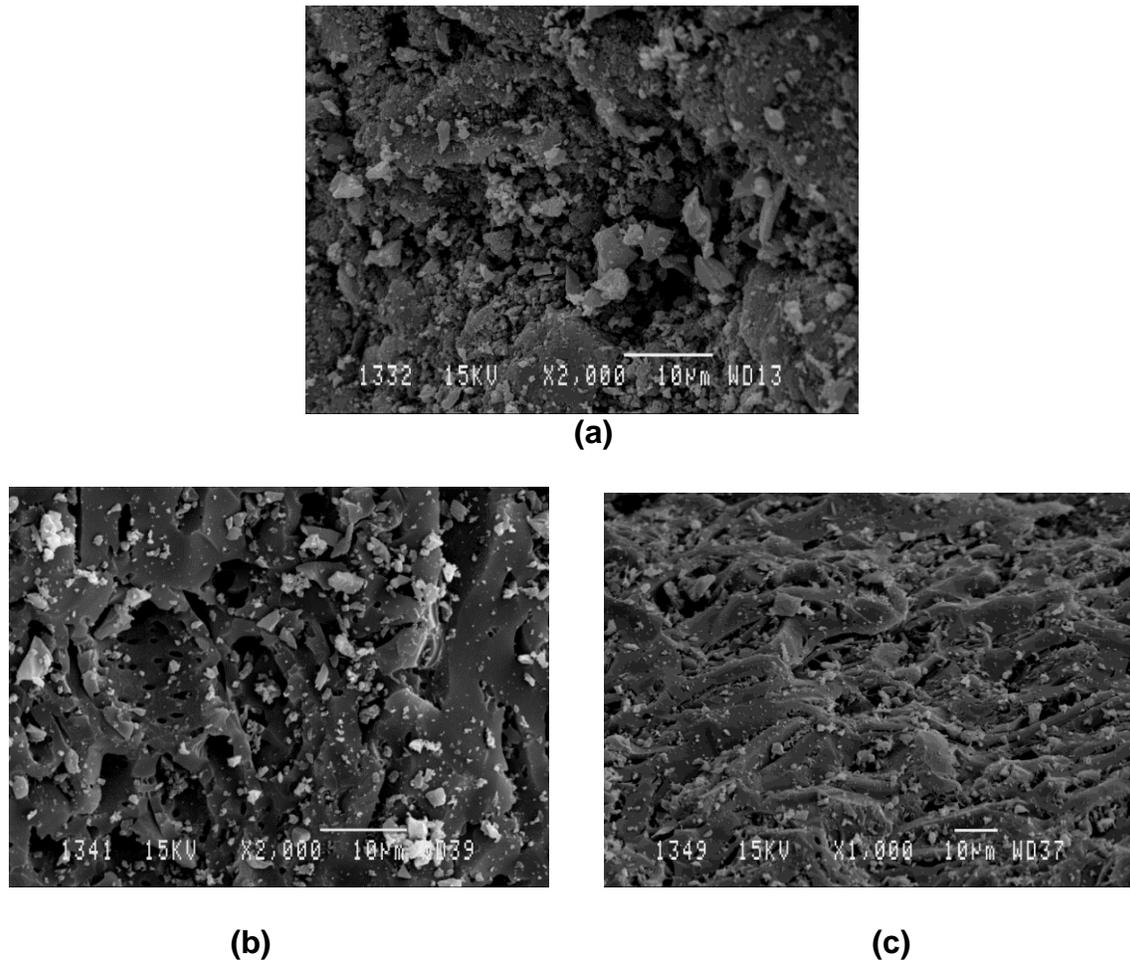


Fig. 2. Scanning electron micrograph of (a) CAC0, (b) CAC8 and (c) CAC36.

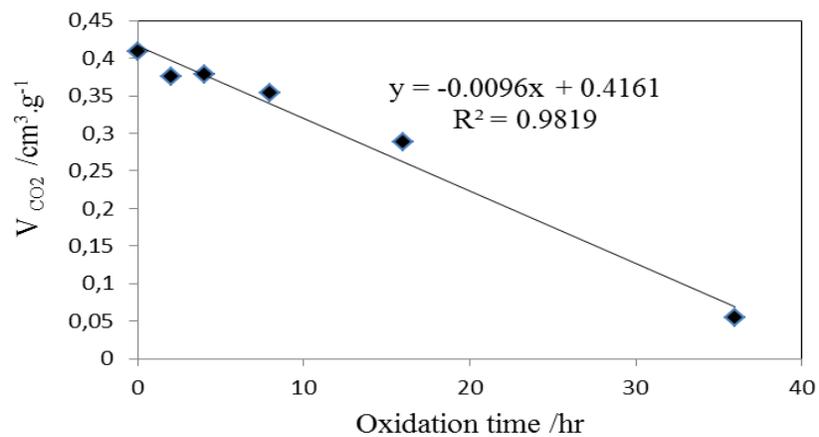


Fig. 3. Variation of V_{CO_2} against the oxidation time

Surface Chemistry

Infrared spectroscopy

FTIR spectra of sample CAC0 and its two oxidized derivatives CAC2 and CAC8 are depicted in Fig. 4. The broad and intense shoulders at 3500 cm^{-1} , seen in the three spectra, are associated with the stretching vibrations of hydroxyl groups involved in hydrogen bonding, probably with the participation of water adsorbed on the carbon (El-Hendawy 2003; ShamsiJazeyi and Kaghazchi 2010). The bands within the range from 1700 to 1200 cm^{-1} were more intense after oxidation. The band at 1700 to 1710 cm^{-1} is generally ascribed to the stretching vibrations of C=O bond in carboxylic acid and lactone groups (Boehm 2002). However, the peak at 1600 cm^{-1} is attributed to a quinone structure. Finally, the band at 1250 cm^{-1} has been assigned to C-O stretching and O-H bending modes of alcoholic, phenolic and carboxylic groups (Shen *et al.* 2008).

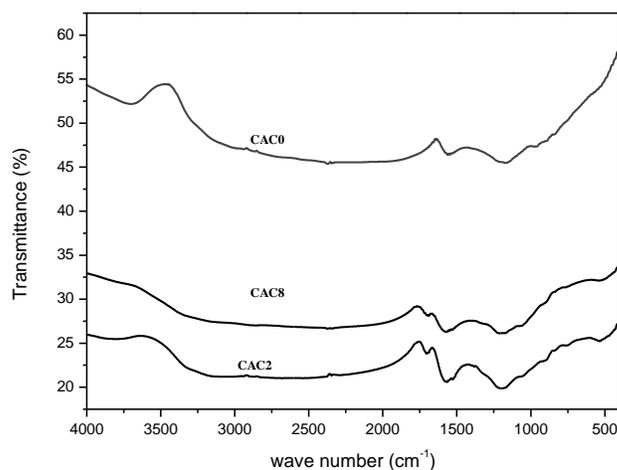


Fig. 4. FTIR spectra for virgin and some oxidized samples

Boehm method and pH_{PZC}

The results of the Boehm titration method and pH of zero charge are reported in Table 2. The values indicate that the sample CAC0 has only an acidic character. This is probably due to the use of phosphoric acid as an activating agent. Moreover, CAC0 is characterized by possessing low content of lactones, and a much greater amount of phenol and carboxylic groups.

The treatment with nitric acid during different reflux times enhanced considerably the number of oxygenated acidic surface groups such as carboxyls, lactones, and phenol. This was expected, as HNO_3 in aqueous solution is a strong mineral acid that may then oxidize carbon atoms and cause the carbon surfaces to lose its electrons and acquire positive charges. Simultaneously, oxygen anions existing in the solution would be adsorbed to form surface oxides. This phenomenon has been observed before and is considered by different authors (Wibowo *et al.* 2007; Pereira *et al.* 2010). However, these created groups don't increase by the same factor. After 16 hours of oxidation, lactone groups increase 11 times compared to the untreated carbon, while phenol and carboxyl

groups increase after 36 hours of oxidation, respectively 1.5 and 2.7 times. This can be related to the high density of carboxyls and phenols on the surface of the untreated sample. On the other hand, Boehm (1994) has reported the conversion of hydroxyl groups to lactones, when they are in close neighborhood. Latter, Domingo-Garcia *et al.* (2002) have explained that a partial condensation of carboxyls and phenols can produce lactonic groups, as the severity of oxidation increased.

Table 2. Chemical Surface Groups (meq.g⁻¹)

Sample	Carboxyl	Lactones	Phenols	Total acid	Basic	Total sites	pH _{PZC}
CAC0	1.45	0.05	0.70	2.20	0.00	2.20	4.00
CAC2	2.10	0.20	1.05	3.35	0.00	3.35	3.82
CAC4	1.90	0.35	1.30	3.55	0.00	3.55	2.91
CAC8	2.00	0.50	1.10	3.60	0.15	3.75	2.50
CAC16	2.10	0.55	1.10	3.75	0.20	3.95	2.00
CAC36	2.25	0.45	1.90	4.60	0.55	5.15	1.84

Unusually, new basic sites were detected after 8 hours of oxidation, and their amounts were still increasing as the acid treatment was extended. This observation is rarely seen after nitric acid treatment, but no clear explanation has been given yet. In our study, this result can be due to the partial titration of the chemical groups, because of high narrow microporosity of our lab-made carbon. The destruction of the narrow microporosity, as a result of oxidation, facilitates the access of the titration probe. In addition, as a result of the increase in surface acidity of activated carbons with oxidation time there was a marked decrease of their pH_{PZC}.

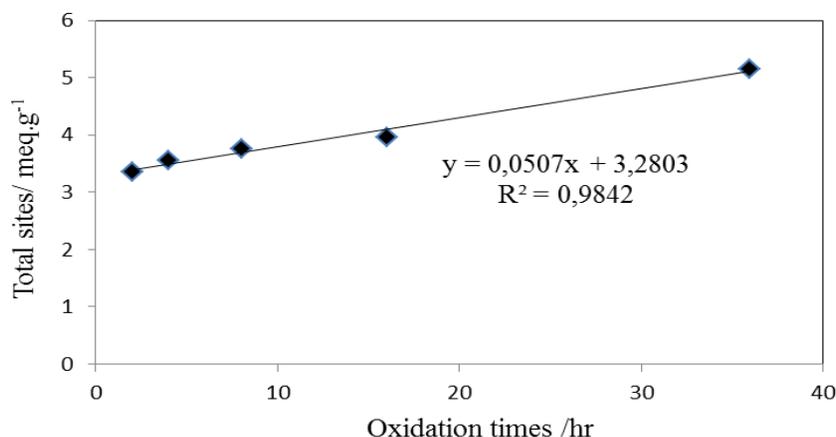


Fig. 5. Evolution of total reactive sites against oxidation times

Interestingly, as displayed in Fig. 5, the total number of functional groups introduced by acid treatment was proportional to the oxidation time. This is a useful tool to determine the theoretical content of surface functional groups, for any oxidation time between 2 and 36 h.

TPD decomposition

The TPD results include the quantification of the CO and CO₂ evolved as temperature increases in a helium atmosphere. This supplies information on the chemistry of the carbon material. The CO₂ evolves at low temperatures (200 to 500°C) as a result of the decomposition of surface groups of an acid nature, whereas the CO comes from weakly acidic, neutral and basic groups, which are more thermally stable and therefore evolve at higher temperatures (400 to 800°C) (Haydar *et al.* 2000). The CO profiles of CAC0, CAC2, CAC8, and CAC36 are depicted in Fig.4. The figure shows that oxidation of carbons by HNO₃ slightly increased the amount of CO-evolving oxygen groups. The majority of the peaks were located at 700°C and 800°C, some researchers attribute them to phenol and quinone groups (Papier *et al.* 1987) and others to ether. Meanwhile, Fig. 5 shows the TPD profiles of CO₂ of the samples cited above. As expected, oxidation of carbons by HNO₃ dramatically increased the amount of CO₂-evolving oxygen groups. After 2 hours of oxidation, there was appearance of many peaks; at 300, 370, 475, and at 632°C. Many authors have reported that such peaks are mostly attributed to carboxylic groups (Boehm, 1994; Tamon and Okazaki, 1996) and to lactones. Table 3 provides quantitative results obtained by integration of the TPD profiles shown in Figs. 4 and 5. The samples desorb more CO than CO₂ which seems to be contradictory with Boehm titration results. This can be related to many reasons according to Boehm (2002); some oxygenated groups such as two adjacent carboxyl groups, lactols, and cyclic lactone can decompose to CO plus CO₂. Furthermore, on microporous carbon, CO₂ can hit the pore walls and form two CO molecules.

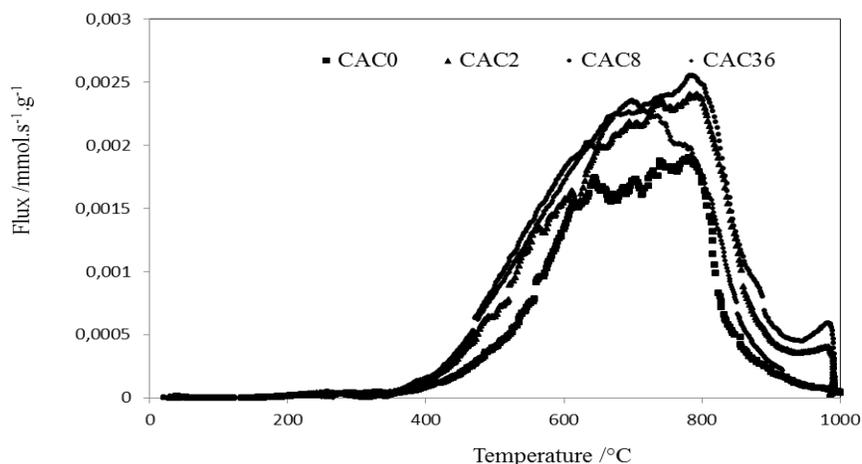


Fig. 6. CO desorption profiles of virgin and some oxidized samples

The amount of desorbed CO and CO₂ increased as the treatment time increased to 8 h. Thus, the amount of atomic oxygen increased. This means that after 8 h the surface

of carbons was saturated and the oxidation did not strongly enhance the creation of new acidic groups. This observation is well confirmed by acid-base titration of Boehm, which demonstrated that the amount of carboxyl groups was almost constant; however the amount of lactone groups decreased and only phenols increased (comparing CAC8 to CAC36). Finally, the CO/CO₂ ratios considerably decreased since the first 2 hours of acid treatment. This can be explained by the formation of double oxygenated functional groups, such as carboxylic acids and lactones after this kind of treatment.

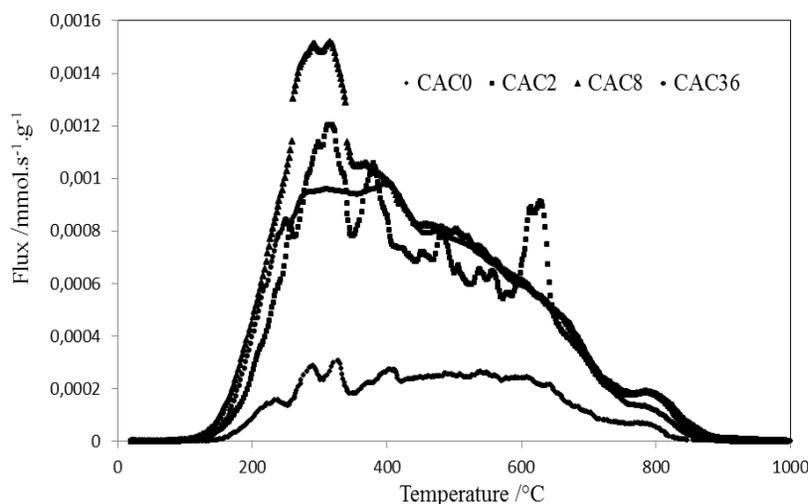


Fig. 7. CO₂ desorption profiles of virgin and oxidized CAC

Table 3. Chemical Surface Groups (meq.g⁻¹)

Sample	CO ₂ (mmol.g ⁻¹)	CO (mmol.g ⁻¹)	CO/CO ₂ (mmol.g ⁻¹)	O (mmol.g ⁻¹)
CAC0	0.715	3.148	4.40	4.578
CAC2	2.457	4.576	1.86	9.489
CAC8	2.805	5.070	1.80	10.680
CAC36	2.587	4.580	1.77	9.754

Liquid Phase Adsorption

Uptake of Pb²⁺ from aqueous solution

The amount of adsorbed Pb²⁺ by raw and modified carbons is listed in Table 4. Compared to other previous works (Kadirveln *et al.* 2008; Sekar *et al.* 2004; Tangjuank *et al.* 2009) the prepared carbon exhibited a considerable Pb²⁺ adsorption capacity (318mg/g). In fact, many researchers (El-Hendawy 2003; Tao and Xiaoquin 2008) show considerable Pb²⁺ adsorption capacity of H₃PO₄-activated carbon. This observation is explained by the presence of phosphor-oxygen complex (POx), which renders the carbon surface slightly polar. Also, these surface oxygen-contained complexes hydrophilic water molecules may ion-exchange with Pb²⁺ (Tao and Xiaoquin 2008). Liquid-phase oxidation

with HNO₃ at different periods enhances the adsorption capacity of CAC0 (up to 330 mg/g). The metal uptake by all activated carbon is improved relatively to that of the untreated carbon. In fact, the carboxylic groups on raw and oxidized carbon produce cation exchange properties (Boehm, 1994).

Since HNO₃-treated carbons showed reduced surface areas, this emphasizes the role played by the surface-chemical nature of the adsorbents. For lead metal its surface complex formation reaction can be explained as follows (Tao and Xiaoquin 2008):



Table 4. Adsorbed Amount of Pb²⁺ on Virgin and Modified Carbons at 30°C

Samples	Adsorption of Pb ²⁺ (mg.g ⁻¹)
CAC0	318
CAC2	323
CAC4	324
CAC8	327
CAC16	328
CAC36	330

Adsorption of 2-nitrophenol from the liquid phase

Adsorption isotherms of 2NP onto raw and modified activated carbon CAC8 are represented in Fig. 7. In general, the two isotherms have similar shape and can be characterized by a rapid increase in the amount adsorbed at low concentrations, and a decreasing slope for higher solute concentration. On the other hand, after the process of strong oxidation leading to a high growth of acidic group content, the sorption affinity of the sample CAC8 towards 2-nitrophenol significantly decreased. The surface oxygen complexes reduce the carbon hydrophobicity and the electron density in the carbon basal planes, thus diminishing the interactions between the aromatic solute and graphene layers. Moreover, the water molecules preferentially form the H-bonds with surface oxygen groups (Joesten and Shaad 1974). These effects result in reduction of the solute adsorption. The linearized Langmuir sorption model was applied to the experimental data. The values of regression parameters and the value of coefficient of determination R², evaluated by least square method, are listed in Table 5. R² values (greater than 0.97) indicate that the isotherms of all the adsorbents can be well fitted by Langmuir model.

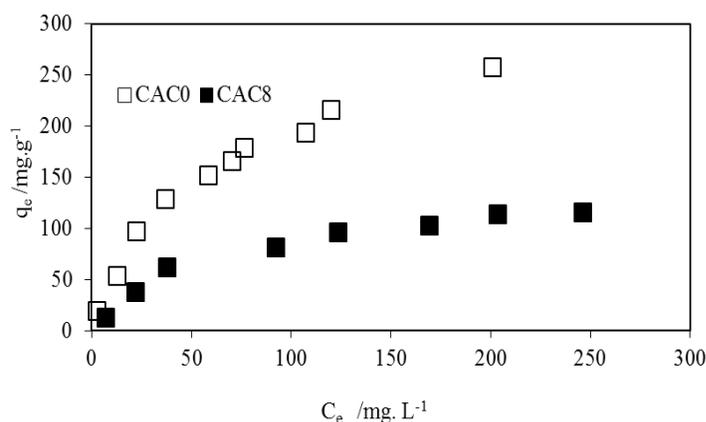


Fig. 8. Adsorption isotherms of 2-nitrophenol (T=30°C).

Table 5. Parameters of Langmuir Model for 2NP Adsorption on Virgin and Modified Carbon Samples

Sample	q_m (mg.g ⁻¹)	K_L (L.g ⁻¹)	R ²
CAC0	312	0.018	0.992
CAC8	147	0.015	0.978

CONCLUSIONS

1. H₃PO₄ activation of olive stones leads to highly microporous carbon, with a microporous framework.
2. Nitric acid oxidation of carbon leads to the introduction of considerable amount of oxygenated surface groups, especially lactones, from the first two hours of oxidation.
3. During the treatment time, the total amount of reactive sites (acid and basic groups) remains linear. This demonstrates the importance of time on controlling nitric acid oxidation.
4. The framework of the treated carbons is not altered considerably even after extended treatment. Narrow porosity is the most affected parameter and it shows proportionality toward oxidation time.
5. The raw carbon shows an excellent potential in adsorbing Pb²⁺. Oxidation enhances this capacity, as a result of improving its cation exchange properties.

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