J. Chil. Chem. Soc., 64, Nº 1 (2019)

ENHANCED ADSORPTION OF PHENOL USING ALKALINE MODIFIED ACTIVATED CARBON PREPARED FROM OLIVE STONES

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ABSTRACT

Activated carbon (AC) prepared from olive stone (OSAC) was modified separately by ammoniac (OSAC/AM) and sodium hydroxide (OSAC/H) aqueous solutions impregnation in order to improve their adsorption properties toward phenol. The raw and modified activated carbons were characterized. The porous structure was characterized using N_2 adsorption at 77 K. The surface functional group characteristics were examined by Fourier transform infrared (FTIR) spectroscopy, Boehm titration, the point of zero charge (pH_{pzc}) measurement and X-ray photoelectron spectroscopy (XPS) method. The isotherms of phenol adsorption on the original and modified ACs were measured. After modification, the activated carbon showed enhanced adsorption capacity for phenol. The effect of alkaline solution concentration on adsorption process was investigated. Results showed a decrease of the microporosity of AC after alkalin treatment especially for higher solution concentration. The amounts of the surface basic groups of the modified ACs increased, in comparison with the original AC, with the increase of the alkaline concentration; however the acidic surface groups decreased. The equilibrium adsorption data were best described by Langmuir model. The maximum adsorption capacity of phenol enhanced for ammonia and sodium hydroxide, respectively, compared with the original AC. We noted that the higher alkaline concentration the higher the adsorption capacity of AC for phenol.

Keywords: Activated carbon, alkaline solution, surface functional groups, porosity, phenol adsorption.

1. INTRODUCTION

In recent years wastewaters has became an increasing concern and represent a serious potential hazard for human health and aquatic life. Phenolic compounds are indeed very toxic, with a fixed low admissible level of 0.5mg/L of water [1, 2].

Activated carbon has received considerable attention as a means of preventing the emission of pollutants into the environment; it is the most common adsorbent for gases, liquids and solutes in solution [3, 4]. The adsorption capacity of these adsorbents depends primarily on the extent of their surface area and on the nature of the porosity [5] and secondly it depends on the surface functions [6]. Numerous precursors have been used with success for the preparation of activated carbons including peat [6], bagasse [7], sawdust [8], plants [9, 10], sludge [11], rice bran [12], husk [13], fruit peel [14], waste tee [15], and coffee grounds [16]. An important reason to select these raw materials is their low cost as this is a relevant parameter in the activated carbon production.

The surface chemistry of carbon materials is basically determined by the acidic and basic character of their surface [17] and can be changed by treating them with alkaline solution or with oxidizing agents either in the gas phase such as air [18], ozone [19, 20] or in solution such as sulfuric acid [21], nitric acid [22] hydrogen peroxide [23, 24], chlorine water [25]. A given treatment will modify the pore structure and the chemical nature of the activated carbon surface. The extent of the modification being a function of the type of the oxidizing agent applied and the surface characteristics of the carbon [26].

The primary objective of this study is to discuss phenol adsorption capacity of H_3PO_4 activated olive stone carbon and basic surface modified activated carbons. The effects of important factors such as the concentration of basic solutions and the surface functional groups of the adsorbents on the equilibrium capacities are discussed. The textural modifications are carried out by means of the adsorption of N_2 at 77 K. The changes in the chemical structure of the samples are analyzed by the Boehm titration methods. The phenol molecule is adsorbed into the different AC samples.

2. MATERIALS AND METHODS

2.1. Preparation of activated carbon by chemical activation

Olive stone, used as raw material is a by-product disposed in a considerable amount by Tunisian oleic industries. It was washed with distilled water to remove dust and dried at 60°C for 24h. Olive stone was impregnated with 50% (w/w) phosphoric acid solution. The mixture was boiled under reflux during 9h. After that, it was filtered and the impregnated sample was dried at the ambient temperature for 24h. The impregnated sample was set in a vertical stainless steel tubular reactor. The impregnated sample was carbonized under a nitrogen gaz flow at temperature of 170°C during 30 min and at a temperature of 410°C during 2h 30 min. After heating, the system was cooled down to room temperature under the same flow of nitrogen and the product obtained was washed with distilled water until pH 6. The washed sample was then dried for 4h at a temperature of 110°C and indicated as OSAC.

2.2 Alkalis modification of activated carbon

Activated carbon was treated with alkaline solutions. Four different concentrations (1, 2, 3 and 4M) of ammonia and sodium hydroxide solutions was used. For this purpose, 30 g of AC were mixed with 250 mL of alkaline solution and the mixture was boiled for 3 h. Then, the treated carbons were washed to eliminate the basic solution excess. Finally, the samples were dried at 110 °C. The samples so prepared with ammonia were labeled OSAC 1M/AM, 2M/AM, 3M/AM and OSAC 4M/AM respectively, and ACs treated with sodium hydroxide are OSAC 1M/H, 2M/H, 3M/H and OSAC 4M/H. The treated carbons were washed with distilled water until attaining a constant pH value of the washing water then dried at 110°C for 24h.

2.3. Characterization methods

2.3.1 Textural characterization

The surface area of the OSAC was determined from the N_2 adsorption isotherms conducted in a volumetric apparatus (ASAP 2020, Micromeritics). Adsorbents were degassed at 130°C for 15 h prior to adsorption experiments. One hour of equilibrium time was allowed for each point of N_2 adsorption. The textural characteristics have been determined by applying the BET [27] and Dubinin–Radushkevich (DR) [28] equations to the isotherms.

2.3.2 Acid / base titrations

The amounts of functional groups were determined by Boehm method [29]. The reagents used were HCl, NaOH, $NaHCO_3$, Na_2CO_3 and $NaOC_2H_5$ solutions. About 1 g of a sample was placed in five separate glass bottles containing 50 ml of 0.1 N solution of each reagent above mentioned. The bottles were gently shaken for 72 hours. The solutions were then filtered using filter paper. The amount of each reagent adsorbed was determined by back titration of the solution. Hydrochloric acid was the titer for the basic solutions, and sodium hydroxide was used to titrate the hydrochloric acid solution.

2.3.3 pHpzc titrations

The pH of the point of zero charge (pHpzc) is the pH above which the total surface of the carbon particles is negatively charged. It is measured by the so-called pH drift method. Accurately weighed portions of each carbon 0.15g were filled into conical flasks containing 50 mL of 0.01 M NaCl standard solutions. The initial pH of these solutions were varied (pH 2-12) and then shaken mechanically for 48 hours. Initial pHs were adjusted by adding either HCl or NaOH (0.1M). After a period of 48 hours shaking, the final pH values of the suspensions were determined using a Mettler- Toledo 340 pH-meter. The final pH values were plotted against the initial pH values and the pH at which the curve crosses the line pH(final) = pH(initial) is taken as the pHpzc of the given carbon.

2.3.4 Fourrier transform infrared spectroscopy

The nature of the surface functional groups has also been analyzed by the transmission infrared spectra obtained from a Fourier transform

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spectrophotometer (Mattson 5000 spectrometer). Data acquisition was performed automatically using an interfaced computer and a standard software package. The samples were dried under vacuum at 150°C prior to mixing with KBr powder. For this purpose, wafers of KBr containing about 0.5% of sample were prepared. They were dried overnight at 393 K before the spectra were obtained. The spectra were recorded between 400 and 4000 cm^{-1}.

2.3.5 X-ray photoelectron spectroscopy (XPS)

Analyses were performed, in order to investigate the surface chemical composition. The C1s line at 284 eV was used as the internal reference. XPS has been shown to be a useful tool for analyzing the surface groups of activated carbons. It allows for semi-quantitative analysis of functional groups by examining the shift in binding energies and thus the local chemical state [30, 31]. The binding energy increases when more electron density is withdrawn from the electron shell; thus not only the number of bonds to other atoms is essential but their electronegativity. XPS can provide valuable information from the atomic concentrations which were determined from the integrated peak areas of the C1s, O1s and N1s core-level spectra and their respective sensitivity factors.

2.4. Adsorption isotherms

The study of phenol adsorption took place in a constant temperature bath (30°C) under continuous shaking. This molecule was obtained from Prolabo with purity higher than 98%. A stock phenol solution was prepared initially at concentration of 1g/L, using bidistilled water. Equilibrium experiments were carried out by the placement of a given amount of activated carbons in 250 mL Erlenmeyer flasks and addition of a volume of 200 mL with variable concentration of phenol solution. The mixtures were then shaken for 4 hours considered adequate to reach equilibrium. At the end of time, the content of each flask was filtered and the filtrate was analyzed by a UV-spectrophotometer at 270 nm.

The equilibrium adsorption amount, q_e (mg/g), was calculated by:

$$q_e = \frac{C_0 - C_e}{m_{AC}} \cdot V \qquad (1)$$

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; m_{AC} (g) is the weight of AC.

Three isotherm models namely Langmuir, Freundlich and Tempkin isotherm were examined. Linear regression was used to determine the best fitting model. The Langmuir model supposes that adsorption occurs uniformly on the active sites of the adsorbent surface. Once the adsorbate occupies an active site, no further adsorption can take place at this site. The Langmuir adsorption equation is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (2)$$

Where, qe is the amount adsorbed (mg/g) at equilibrium. Ce is the equilibrium solution concentration (mg/L). q_m and K_L, the Langmuir constants represent the maximum adsorption capacity (mg/g) at complete monolayer coverage and energy of adsorption respectively. The plot of Ce/qe vs Ce is a straight line from the slope and intercept of which the Langmuir constants can be determined. The essential characteristics of the Langmuir isotherm can be made on the basis of a dimensionless equilibrium parameter, R^2, also known as separation factor is given by:

$$R^2 = 1 /(1 + K_L C_0) \qquad (3)$$

Where C_0 is the initial dye concentration and K_L is the Langmuir constant. This parameter can indicate whether the adsorption process is irreversible ($R^2=0$), favorable ($0<R^2<1$) linear ($R^2=1$) or unfavorable ($R^2>1$).

3. RESULTS AND DISCUSSION

3.1 Textural characterization

In order to estimate the structure parameters characterizing the activated carbon and to study the influence of its modification on the changes of pore structure, adsorption isotherms of nitrogen at 77 K were measured. Comparing the results one can find some differences in the pore structure of analyzed carbons being a result of the modification methods. The nitrogen adsorption isotherms at 77 K, shown in Figure 1, are of type I in the International Union of Pure and Applied Chemistry Classification. It is evident that most of the pore volume of the samples is filled below a relative pressure of about 0.1, indicating that these samples are highly microporous. According to this figure, the treatment with alkaline solution slightly decreases the adsorption capacity of the samples. The isotherms of the non-treated carbon, OSAC and those of OSAC/H and OSAC/AM show a fast increase in the adsorption at low relative pressures and a round elbow of the plot, which is typical of solids with a homogeneous microporosity.

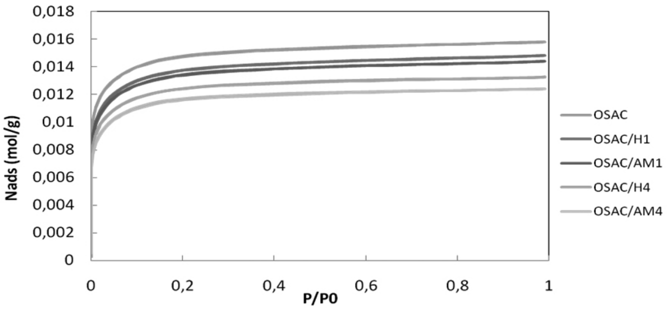


Figure 1 : Nitrogen adsorption isotherms of the OSAC before and after alkaline treatment.

Table 1 presents the results of characterization of all samples.

Table1: *Pore structure characteristics of raw and modified carbon samples.*

Charbon actif		BET Surface area (m^2/g)	Micropore volume (cm^3/g)	Average pore diameter (Å)
OSAC		1165	0,531	20,86
OSAC/H	1M	1144	0,46	20,72
	2M	846	0,39	21,4
	3M	756	0,339	21,4
	4M	649	0,27	22,1
OSAC/AM	1M	729	0,337	20,97
	2M	613	0,28	21,3
	3M	549	0,26	22,5
	4M	541	0,201	22,85

The modification process led to overall increase of the pore diameter of the carbon sample, this may be due to the reduction in micropore volume of MTLAC after modification (Table 1). It can be seen that treatment with sodium hydroxide (1M) does not significantly modify specific surface area of activated carbon however a large decrease of micropore volume is observed. Ammonium (1M) treatment leads to an appreciable loss of the surface area, from 1165 m^2/g to 729 m^2/g, as well as a decrease of the micropore volume from 0.531 cm^3/g to 0.337 cm^3/g. Also alkalin treatment leads to a decrease of the surface area of the AC from 1165 m^2/g for the raw AC to 649 m^2/g for sodium hydroxide (4M) treated AC and to 541 m^2/g for ammonia (4M) treated adsorbent. The loss of micropore volume from 0.531 to 0.27 cm^3/g for OSAC 4M/H and to 0.2 cm^3/g for OSAC 4M/AM indicates that basic treatment reaction occurs mainly in the microporous region. The lowest adsorption of nitrogen is observed for the OSACs treated with 4M concentrated sodium hydroxide solution and ammonia at elevated temperatures. It may be attributed to the significant amount of the oxygen containing groups introduced by the treatment with alkalis which have been probably fixed in the most active sites at the entrance of the micropores that could block smaller micropores and decrease as a result the adsorption space accessible for nitrogen molecules [32]. As consequence, the volumes of adsorption are smaller.

3.2 Surface functional groups : Boehm titration

The Boehm titration method allows the determination of the surface functional groups such as phenolic group (–OH), lactone group (C=O), carbonyl and carboxylic group (–COOH). The amounts of surface functional groups of raw and treated OSACs were presented in Table 2.

Table 2: *Chemical surface groups (meq.g^{-1})*

Sample	CG[a]	L[b]	H[c]	CaG[d]	TAG[e]	TBG[f]	pH pzc[g]
OSAC	0,35	0,29	0,61	0.03	1.27	0.26	2.1
OSAC 1M/H	0,33	0,25	0,65	0.02	1.25	0,25	7.3
OSAC 2M/H	0, 29	0,19	0,71	0,01	1.2	0.30	8.2
OSAC 3M/H	0.23	0,15	0.82	0,01	1.21	0.33	8.6
OSAC 4M/H	0.15	0,09	0.92	0	1.16	0.42	8.85
OSAC 1M/AM	0,33	0,22	0,63	0,03	1.19	0,28	7.1
OSAC 2M/AM	0,28	0,15	0,73	0.02	1.18	0.32	7.4
OSAC 3M/AM	0.15	0,1	0,84	0,01	1.1	0.35	8.1
OSAC 4M/AM	0.11	0.09	0.89	0	1.09	0,43	8.6

[a] Carboxylic groups
[b] Lactones
[c] Hydroxyl groups
[d] Carbonyl groups
[e] Total acidic groups
[f] Total basic groups
[g] pH of the point zero charge

Results show that the acidic nature was dominating in the surface chemistries of all ACs, however, the basic nature of treated OSAC increased substantially with the rise of concentration. For virgin activated carbon (OSAC), the total acid oxygen containing group is 1.27 meq/g and the basic is 0.26 meq/g. When treated with NaOH (4 M), the basic functional group increases to 0.42 meq/g which is an increase of 61.53% compared to the untreated OSAC. Increase in oxygen containing functional groups, takes mostly in the phenolic categories. The phenolic group increases from 0.61 to 0.92 meq/g. Actually this results were found by Chiang et al. [33] who treated AC with NaOH (1–5M), they noted that the major increase takes place in the phenolic group so to explain this results they used the following reaction between NaOH and activated carbon:

$$C + 6OH^- = CO_3^{2-} + 3H_2O + 4e^- \qquad (2)$$

$\Delta G^0 = -70.72$ kcal / mole.

It is further known that

$$4H^+ + O_2 + 4e^- = 2H_2O \qquad (3)$$

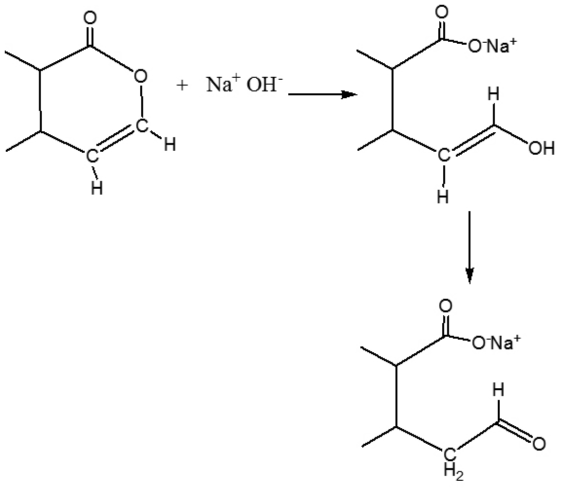
$\Delta G^0 = -113.38$ kcal / mole

Combining equations (2) and (3), one has

$$C + 2OH^- + O_2 = CO_3^{2-} + H_2O$$

$\Delta G^0 = -184.10$ kcal / mole

The following shows the conceptual scheme of NaOH reaction with activated carbon:



Treatment of AC with ammonia (1– 4M) increases the total concentration of the basic functional groups from 0.26 meq/g to between 0.28 and 0.43 meq/g, dependent on the solution concentration. This is an increase of almost 7.7 – 65.38%. As far as the individual oxygen containing functional groups are concerned, the phenolic group increases from 0.61 to between 0.63 and 0.89 meq/g. Like sodium hydroxide-treated activated carbon, the major increase takes place in the phenolic group. This result clearly demonstrated the strong effect of basic treatment on enhancing the basic nature of OSACs. The redistribution of surface functional groups of OSAC/AM and OSAC/H was caused by the strong interaction between alkalin treatment and the original surface functional groups of OSAC. The pHpzc was one of the most important surface chemical properties of OSAC, which corresponded to the pH value of the solution surrounding OSAC when the sum of surface positive charges could balance the sum of surface negative charges. The effects of pHpzc on the surface acidity were summarized as follows: when OSACs were introduced into an aqueous environment, their surface charges were positive if solution pH < pHpzc and were negative if solution pH > pHpzc; when solution pH was equal to the pHpzc of OSAC, the surfaces of OSACs were electrically neutral. The pHpzc values of raw and treated ACs were measured and the results were presented in table 2. As could be seen in this table, the modified ACs exhibited higher pHpzc which increased with the rise of the basic solution concentration. This result indicated that higher amounts of basic groups were formed on the surfaces of OSAC/AM and OSAC/H than that of raw AC, which should be responsible for the increase in pHpzc values.

3.3 Surface functional groups – IR analysis

Figure 2 shows FTIR spectra of the OSAC/H treated at different concentration of basic solutions.

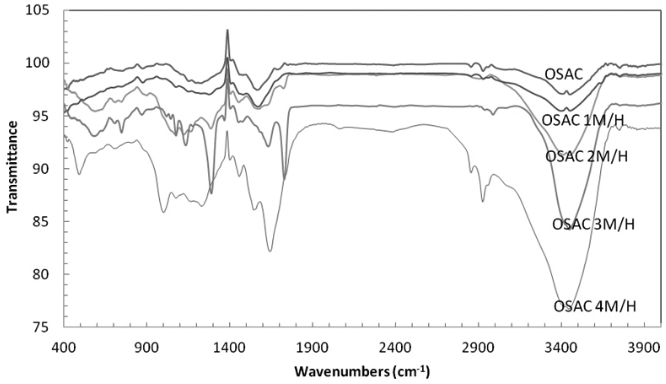


Figure 2: FT-IR spectra of the untreated activated carbon (OSAC) and NaOH treated activated carbons.

Four mains peaks were detected on the spectra of sodium hydroxide modified activated carbons. The first is at bandwidths around 3410–3434 which could be assigned to O–H stretching vibration of hydroxyl functional groups. The spectrum of the OSAC/H exhibits one strong peak at 1536 cm^{-1} associated with C–O group whereas peak at 858 cm^{-1} was attributed to P–O–C carbons asymmetric stretching, interaction between aromatic ring vibration and P–C (aromatic) stretching and/or symmetrical stretching of PO_2 and PO_3 in phosphate–carbon complexes. Therefore, P-containing carbonaceous structures like acid phosphates and polyphosphates are formed in the samples carbonized in the presence of H_3PO_4 [34]. The last peak is seen at 2920 -2898 cm^{-1}, which was due to asymmetrical and symmetrical stretching of CH_2.

On the other hand, the spectra of ammonia- modified samples (figure 3) shows some differences.

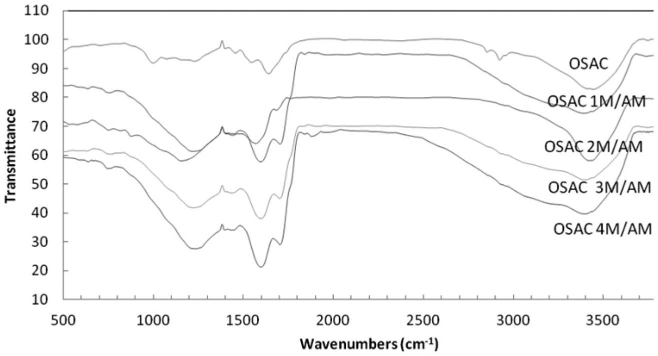


Figure 3: FT-IR spectra of the untreated activated carbon (OSAC) and NH_3 treated activated carbons.

Note there are three peaks that are present at the spectrum of OSAC/AM which exhibits the appearance of new bands related to N-containing species. The first is a peak at 1542 cm^{-1} (cyclic amides [35]) and the second is at 1052 cm^{-1} (C–N of the amine group [35]) implying that the use of ammonia modification produced new nitrogen surface complexes. The results were comparable with the work done by Przepiórski [36] which reported that more basic groups such as cyclic amides and amines groups were produced by ammonia-treated activated carbons. Finally, a peak occurs at 3560 cm^{-1} for the corresponding OH stretching.

3.4 Surface functional groups – XPS

XPS analysis was performed to determine the chemical modification of OSAC before and after alkaline treatment. Table 3 and 4 show the effect of basic solution concentration on the contents of carbon, oxygen and nitrogen on OSAC surfaces.

Table 3: *Surface elemental analysis of untreated and NaOH treated OSAC using XPS*

Sample	C (at.%)	O (at.%)	P (at.%)
OSAC	92.37	6.55	1.08
OSAC 1M/H	92.7	6.90	0.41
OSAC 2M/H	94.37	5.22	0.41
OSAC 3M/H	92.16	7.64	0.19
OSAC 4M/H	91.02	8.39	0.59

Table 4: *Relative area (%) of C1s, O1s XPS for the untreated and NaOH treated OSAC*

Sample	C1s				O1s		
	284.4 (eV)	285.5 (eV)	286.8 (eV)	288.9 (eV)	530 (eV)	532.5 (eV)	533.4 (eV)
OSAC	66.68	21.11	3.93	7.05	55.03	34.22	10.75
OSAC 1M/H	66.77	19.66	6.01	5.69	58.01	29.3	12.69
OSAC 2M/H	73.81	12.61	8.47	2.44	38.63	47.26	14.11
OSAC 3M/H	74.87	11.3	7.34	3.96	49.82	44.48	5.7
OSAC 4M/H	74.26	12.08	6.28	4.85	51.57	44.16	4.27

The C1s peaks are deconvolved into four component Gaussian and Lorentzian peaks [37]. The main peak (1) at 284.4±0.2 eV corresponds to the sp^2 hybridized graphite-like carbon atoms (C=C). Table 4 shows that besides graphitic carbon, there is a peak (2) centered at 285.5±0.2 eV is attributed to the sp^3 hybridized carbon atoms (C–C). Peaks (3) at 286.8±0.2 eV and (4) at 288.9±0.2 eV correspond to C–O (e.g., alcohol, and ether), and O–C=O (e.g., carboxylic, and ester) functionalities, respectively.

The quantitative analysis indicates that the NaOH treatment leads to a decrease in the sp^3 C-C content from 21.11% for the untreated OSAC to 11.3 % for the OSAC 3M/H however a slight increase is shown for OSAC 4M/H (12.08%). In the other hand the C=C content increase from 66.68 % to 74.26 % for OSAC 4M/H comparing to the untreated AC.

Concerning the oxygenated groups, as we can see the carboxylic groups (O–C=O) decrease from 7.05% to 2.44% for activated carbon treated with 2M concentrated sodium hydroxide, but increase again for OSAC 3M/H and OSAC 4M/H.

An increase in the C–O components for activated carbon, treated with different concentration of sodium hydroxide solution, comparing to the raw AC.

Three different oxygen functional groups, as reported in the studies of Huang et al. [38]. The peak at 530.6 eV corresponds to the carbonyl oxygen atoms in esters, amides and anhydrides as well as oxygen atoms in hydroxyls or ethers (carbonyl); the peak at 532.5 eV to the ether oxygen atoms in esters and anhydride (ether); and the peak at 533.4 eV to the oxygen atoms in the carboxyl groups (carboxyl).

As shown in table 4, the carbonyl (530.6 eV) and carboxyl (533.4 eV) groups that have C=O double bond, increase slightly for 1M and 2M treated AC then decrease remarkably after treatment with 3M and 4M sodium hydroxide solution. Actually carboxyl group decrease from 10.75% to 4.27% for OSAC 4M/H. For ether and groups that have –OH bond (532.5 eV) they increase from 34.22% to 44.16 % comparing to the original activated carbon. These results agree well with Boehm which indicated that carboxylic oxygen groups decrease after alkalin treatment while phenolic groups increase.

The surface atomic compositions obtained by XPS analysis of samples treated with ammonia are presented in table 5.

Table 5: Surface elemental analysis of untreated and NH_3 treated OSAC using XPS.

Sample	*O (at.%)*	*C (at.%)*	*N (at.%)*	*P (at.%)*
OSAC	6.55	92.37	0	1.08
OSAC 1M/AM	19.9	76.66	2.92	0.52
OSAC 2M/AM	12.74	85.10	1.39	0.77
OSAC 3M/AM	18.81	79.28	1.7	0.21
OSAC 4M/AM	18.73	78.32	2.68	0.63

It can be seen that the surface of the OSAC/AM is mainly composed of carbon, oxygen, and nitrogen. It is found that all surface functional groups containing C=O increased after the treatment with 4M ammonia solution comparing to raw AC. For OSAC/AM the C1s peaks are deconvolved into four components Gaussian and Lorentzian peaks same as for OSAC/H but in different percentage shown in table 6.

Table 6: Relative area (%) of C1s, O1s XPS for the NH_3 treated OSAC.

Sample	C1s				N1s				O1s	
	284.4 (eV)	285.5 (eV)	286.8 (eV)	288 (eV)	398 (eV)	399.5 (eV)	400 (eV)	402 (eV)	529.5 (eV)	531.6 (eV)
OSAC 1M/AM	50.09	35.57	13.23	0.8	23.62	0	75.61	0.77	22.86	77.14
OSAC 2M/AM	56.22	19.8	15.17	5.53	0	5.39	94.61	0	38.45	61.55
OSAC 3M/AM	44.56	38.57	13.55	1.89	0	24.61	75.93	0	11.87	88.13
OSAC 4M/AM	56.62	28.26	12.88	1.16	0	10.74	89.26	0	29.23	70.77

The O1 s peaks are deconvolved into two component Gaussian and Lorentzian peaks [39,40]: Peaks (1) at 529 ±0.2 eV and (2) at 531 ±0.2 eV correspond to C=O and C-O species, respectively. The ratio of peak area of C–O decreases from 77.14% to 70.77% after ammonia treatment in spite of an increase to 88.13% for OSAC 3M/AM.

The high-resolution XPS spectra of the N1s region are illustrated in figure 4.

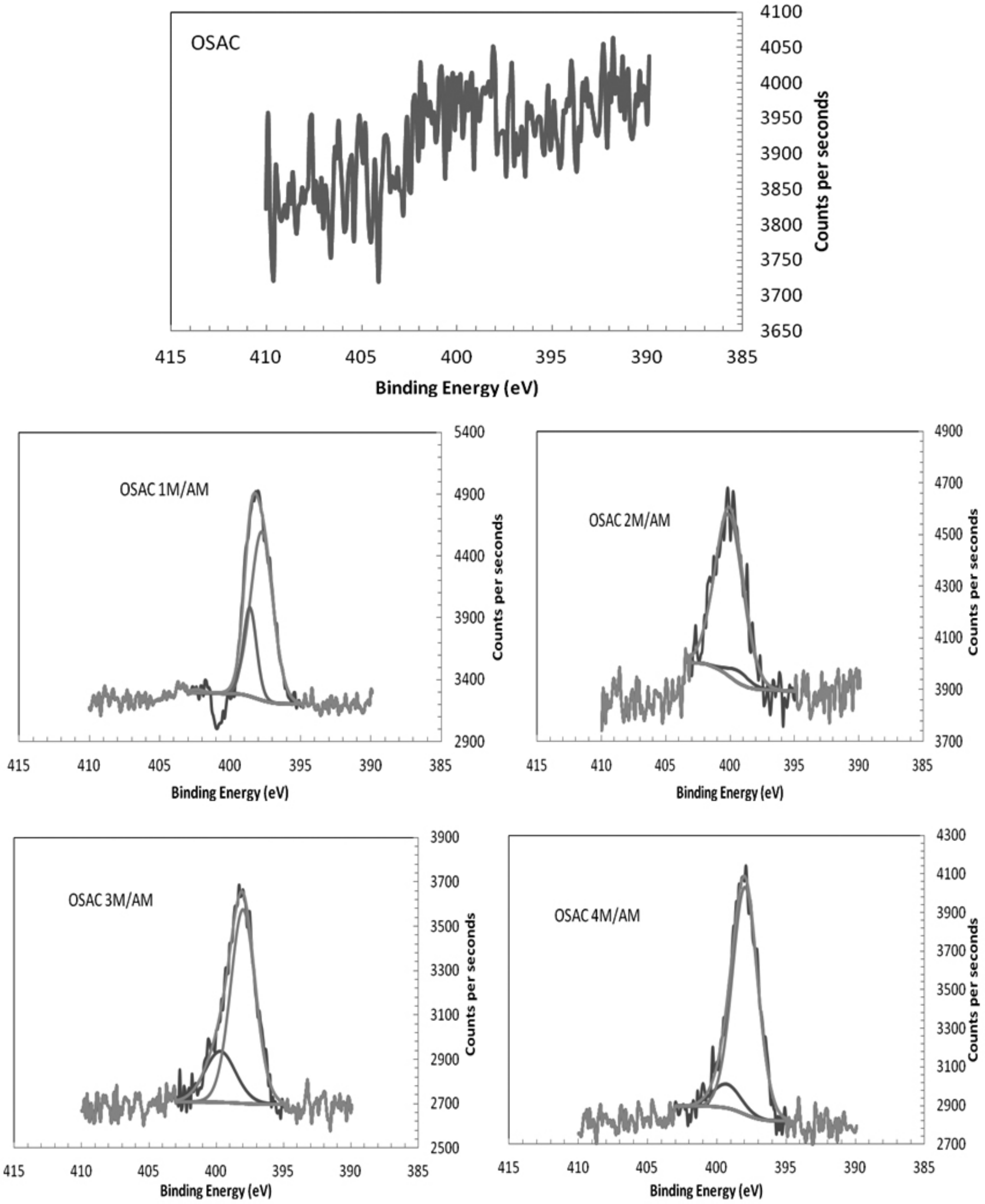
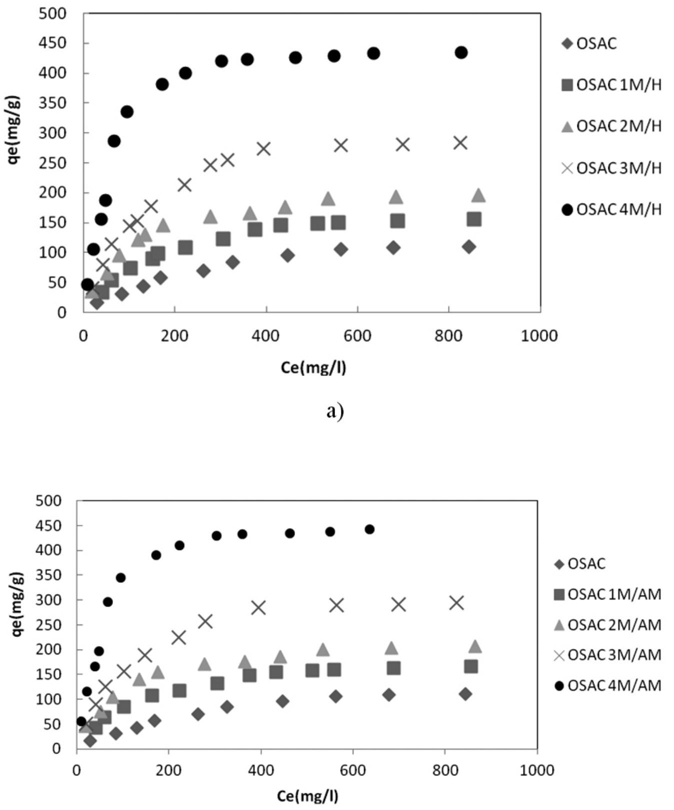


Figure 4: Representative N1s spectra of OSAC (a), OSAC 1M/AM (b), OSAC 2M/AM (c), OSAC 3M/AM (d), OSAC 4M/AM (e).

From previous researchers [41], the following assignments were made: pyridine 398 eV, amides 399.5 eV, aromatic amines $–NH_2$ aniline and/or imines C=NH 400 ± 0.2 eV and quaternary nitrogen 402 eV [42–43]. Nitrile groups would be unlikely to remain on the surface as they are prone to electron assisted desorption [43]. The curve fitting of the raw data allowed the percentages of each group to be calculated and displayed in table 6. Above 2M there was an increased amount of amide at 399.5 eV from 0 to 24.61% for OSAC 3M/AM, although this amount decrease for AC treated with 4M concentrated ammonia to reach 10.74%. Another increase was observed for aromatic amines $–NH_2$ aniline and/or imines C=NH at 400 eV from 75.61% to 89.26% in spite the decrease for OSAC 3M/AM which is 75.93% . However the decrease of pyridine groups is shown by the reduce of its percentage from 23.62 % to 0% at high concentration of ammonia. These results can be explained this way: ammonia decomposes to free radicals such as NH, NH_2 which can attack the carbon leading to its gasification and the formation of nitrogen functional groups [31]. The reaction of ammonia with carboxylic acids can form an ammonium salt that can be dehydrated to an amide or a nitrile group which explains the increase in amide groups.

3.5 Phenol adsorption isotherms

Results of phenol adsorption on tested activated carbons (fresh and treated with basic solutions) are shown in figure 5 a) and b).



a)

Figure 5: Phenol adsorption isotherms for OSAC treated with different concentration of sodium hydroxide solutions (T=30°C) (a), and for OSAC treated with different concentration of ammonia solutions (b).

And the data plotted according to the Langmuir isotherm are listed in table 7.

Table 7: Parameters of the Langmuir models and maximum experimental quantity for phenols adsorption at 30°C

Sample	q_{exp} (mg/g)	q_{∞} (mg/g)	K_L (L/mg)	R^2
OSAC	110.33	153.84.88	3.42 10^{-3}	0.983
OSAC 1M/H	166,34	192.3	6.07 10^{-3}	0.995
OSAC 2M/H	206,35	222.22	9.12 10^{-3}	0.998
OSAC 3M/H	295,26	333.33	7.94 10^{-3}	0.994
OSAC 4M/H	442,69	476.19	0.0164	0.995
OSAC 1M/AM	156,34	200	0,00584	0,995
OSAC 2M/AM	196,35	250	0,00852	0,998
OSAC 3M/AM	284,26	333	0,00795	0,994
OSAC 4M/AM	435,26	500	0,0157	0,995

We can note that the isotherms present the same form and are of type I of the Giles classification [44]. In comparison with the untreated material, each modified activated carbon demonstrated enhanced adsorption capacity toward phenol. The enhancement in the phenol adsorption depended on the starting concentration of the solution. Hence, adsorption capacities (mg/g) were in the following sequence: 1M < 2M < 3M < 4M. The maxima observed in presented graphs allowed to state that the most distinct enhancement in adsorption of phenol from water occurs for those activated carbons treated with solution concentration of 4M. Furthermore, the highest phenol uptake was observed for OSAC /H. This tendency was seen for all the samples treated with sodium hydroxide independently on the starting concentration of the solution. This means that treatment with sodium hydroxide enhance the phenol adsorption more than ammonia.

It is of common knowledge that for phenols the dominant adsorption factor may be micropore region [45]. There are several other factors that play significant roles in determining the adsorbability of organics onto AC such as the presence of surface functional groups. It is widely recognized that acid oxygen-containing surface groups decrease the adsorption of organic compounds in aqueous solution, while their absence favors adsorption, independently of the polarity of the compounds [46, 47, 48]. As such, while at the elevated concentrations of weakly acidic functional groups on the surface of AC increase their metal adsorptive capacities, the presence of these functional groups seems to be unfavorable for adsorption of phenolic compounds. Results provide by Table 2 show that after alkalin treatment acid oxygen groups decrease (carboxylic acid) and basic functional groups increase which fit well with the results of phenol adsorption. This was also concluded in a study conducted by Leng and Pinto [49] where increased concentrations of surface carboxylic groups were found to decrease physisorption of phenol, possibly due to the increase in water adsorption and weaker dispersion interactions with basal plane carbons. Their research, to a certain extent, reinforced an earlier finding by Mahajan et al. [50] in which the latter argued that phenol adsorption increased when more π electrons were available on the basal plane surfaces of the crystallites and reduced by oxygen complexes on edge sites. Recent studies [51] also justified the aforementioned studies where it was concluded that water is mainly adsorbed on the surface establishing hydrogen bonds with the oxygen groups, which can produce clusters that may block the passage of the adsorptive molecules into the micropores as well as the presence of these oxygen groups reduced adsorptive capacity by localizing free electrons of the carbon basal plane. Other studies [52] suggested the adsorption of some organics on AC was generally determined by π- π dispersion interaction between the electrons of AC surface and the aromatic ring of the adsorbate and by electrostatic interactions between ions attached to the ring and the surface charge of AC. Thus the phenol is regarded as a weak acid, its adsorption becomes unfavorable with the increase in the acid groups number on the surface [53].

Langmuir adsorption equation (2) was applied to experimental isotherms and the corresponding coefficients are given in table 7.

Taking into account the porous structure of the samples tested, the specific surfaces areas of the CAs treated with sodium hydroxide are slightly superior to those of the ammonia-treated ACs. Thus, these materials adsorbed slightly higher amounts of phenol. Similarly, each sample studied showed higher micropore volumes than that of ammonia-treated AC. We know that the adsorption of phenol occurs mainly in micropores and that the molecular diameter of the phenol is 0.62 nm, it can be concluded that the volume of micropores is a factor that influences the capacity of the carbons in the adsorption of phenol. Therefore, in the case of CA modified by the basic solutions, it was also observed that the highest surface area values were observed for CA treated with sodium hydroxide (ranging from 1144 to 649 (m^2 / g), which explains why this material has adsorbed more amounts of phenol than the ammonia-treated CA.

4. CONCLUSIONS

This work demonstrates that selectivity for phenol adsorption can significantly be improved by functionalizing the surface of activated carbon, activated carbon prepared from olive stone by phosphoric acid chemical process was treated by ammonia and sodium hydroxide solutions. Textural and chemical surface properties of raw and modified AC were determined. Results showed that they varied after modification by alkalis. The surface area and pore volume decrease especially when treated with sodium hydroxide. The total oxygen functions groups change after modification, the basic nature of treated OSAC increased substantially with the rise of concentration of basic solutions and quantities of nitrogen functional groups were incorporated into the carbon structure during treatment with ammonia. Variation in surface area and porosity of the adsorbents plays a key role on adsorption of phenol. The adsorption capacity for phenol increased with increase of basic solution concentration. Sodium hydroxyde-treated carbons exhibit higher adsorption capacity toward phenol from water. Taking into account these facts, it was concluded that the increased adsorption capacity results from the changes in surface chemistry of activated carbons occurring during treating with alkalis. Optimized carbon adsorbents for specific organic compounds can be produced by appropriate surface modification.

ACKNOWLEDGEMENT

The authors extend their gratitude to Professor Dr. Fco Javier Lopez Garzon from Granada University of Spain for his valuable assistant in the textural analysis of the activated carbon samples which are BET specific surface area, XPS and FTIR analysis.

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