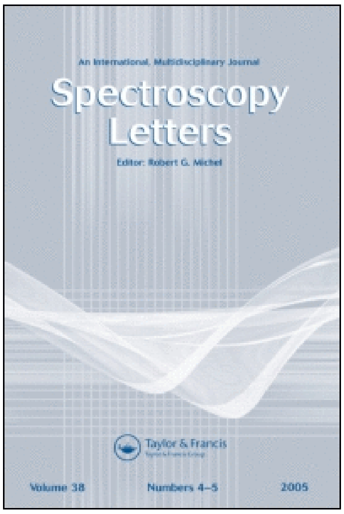

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M. Acedo-Ramos[a]; V. Gomez-Serrano[a]; C. Valenzuela-Calahorro[a]; A. J. Lopez-Peinado[b]
[a] Departamento de Química Inorgánica, Universidad de Extremadura, Badajoz, Spain [b] Departamento de Química Inorgánica, U.N.E.D., Madrid, Spain

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OXIDATION OF ACTIVATED CARBON IN LIQUID PHASE. STUDY BY FT-IR

Key words: Activated carbon, oxidation, surface chemistry, FT-IR

M. Acedo-Ramos, V. Gomez-Serrano, C. Valenzuela-Calahorro
and A.J. Lopez-Peinado*,[1]

Departamento de Química Inorgánica, Universidad de Extremadura,
06071 Badajoz, Spain
*Departamento de Química Inorgánica, U.N.E.D.
28040 Madrid, Spain

Abstract: Surface chemistry of a commercial activated carbon (AC) and of products oxidized in liquid phase using aqueous solutions of a series of oxidizing agents (H_2SO_4, HNO_3, $HClO_4$, H_2O_2, O_3, ClO_2, KIO_4 and $KMnO_4$) has been studied by FT-IR. Oxidation led to surface groups and structures which, and also the extend of formation, depended on the oxidizing agent and the pH and concentration of the solution used. Most oxidizing agents proved to be effective for the formation of surface C=O groups. Variations in pH of solutions of H_2O_2 , KIO_4 and $KMnO_4$ unequally affected the oxidation of AC. This was unfavourable with the increase in concentration of the solutions of HNO_3 and $KMnO_4$. The reverse was noted with KIO_4.

[1] Author to whom correspondence should be addressed

INTRODUCTION

Porous structure and surface chemistry of activated carbons are important properties in connection with its adsorbent behaviour. The surface functional groups further influence in a decisive way the ionic exchange and catalytic and electronic properties of this carbon material (1-5). These facts explain the rising interest in studying the surface chemistry of activated carbon, and especially the carbon-oxygen complexes. Since the pioneering works of Smith (6), Baker (7) and Rhead and Wheeler (8,9), the methods followed in formation of oxygen functional groups and the techniques employed in their study have been very varied. The more frequent methods of introducing surface oxygen in carbons have been oxidation in liquid or gas phases (1). Using the infrared spectroscopy technique, some workers have identified oxygen functional groups of activated carbons. Ishizaki and Marti (10) suggest that some of the surface carbon-oxygen groups are lactonic, quinonic, phenolic and carboxilic groups. Carboxyl, anhydride and cyclic peroxide were also identified (3).

The main objective of this paper is the formation of surface oxygen groups by oxidation of an activated carbon (Merck) in liquid phase using various oxidizing agents in aqueous solutions of varying pH and concentration, and the subsequent study of the surface chemistry of all samples by FT-IR. The infrared technique, despite the very low signal/noise ratio in the case of carbons, has become a powerful tool for identification of surface groups of carbons since the interferometer was incorporated.

EXPERIMENTAL

A commercial activated carbon (supplied by Merck) was the starting material used in this study. The carbon was heat-treated in an ultrapure N_2 flow from room temperature to 960°C, the residence time at maximum heat treatment temperature being 5 h. Subsequently, samples of about 4 g of the resulting material and 50 ml of solution of a given oxidizing agent (H_2SO_4, HNO_3, $HClO_4$, H_2O_2, ClO_2, KIO_4 or $KMnO_4$) were added to a glass flask and the slurry was shaken (70 oscillations per minute) in a thermostatic bath with the water at 25°C. As for O_3, an O_2-O_3 mixture

TABLE 1

Codes of samples, pH and concentration of solutions used for oxidation of AC sample.

Sample*	pH	Concentration	Sample*	pH	Concentration
AC	--	----	$HClO_4$-S	S	2.25M
H_2O_2-S	S	110 vol, 30%	D-KIO_4-S	S	10^{-2}M
H_2O_2-A	A	110 vol, 30%	C-KIO_4-S	S	saturated
H_2O_2-B	B	110 vol, 30%	C-KIO_4-A	A	saturated
O_3-S	S	2.10^{-4}M	C-KIO_4-B	B	saturated
ClO_2-S	S	10^{-2}M	D-$KMnO_4$-S	S	10^{-2}M
H_2SO_4A	A	1.6 10^{-2}M	C-$KMnO_4$-S	S	saturated
D-HNO_3-S	S	10^{-2}M	C-$KMnO_4$-A	A	saturated
C-HNO_3-S	S	14.37M	C-$KMnO_4$-B	B	saturated

* D and C indicate that the solution is diluted or concentrated; S, A and B ,the solution pH, pH = 2.5 and pH = 11.5, respectively (pH was modified adding H_2SO_4 or NH_4OH over oxidant solution).

(2% in ozone; 1167 ml min^{-1}) was bubbled on the bottom of a glass recipient containing 4 g of carbon and 50 ml of distilled water. The contact time of the oxidizing solutions with the carbon was always 5h.

The samples of carbon oxidized with H_2SO_4, HNO_3, $HClO_4$, KIO_4 and $KMnO_4$ were first periodically washed with distilled water for a month with the object of removing the excess of oxidizing agent and the reaction products soluble in water and then oven-dried at 110°C for 24 h. The samples obtained with H_2O_2 , ClO_2 and O_3 were subjected to the latter treatment only. Notations of the samples and the pH and concentration of the solutions used in their preparation are shown in Table 1.

Spectra of AC and oxidized samples were obtained in a Perkin Elmer FT-IR spectrometer, model 1720. KBr was used as diluent and dispersant substance of carbon. The carbon-KBr (ratio = 1:1000) mixtures were first ground in an agate mortar and then pressed at 10 tons during 3 min in a Perkin Elmer hydraulic press. The resulting pellets were oven-dried at 110° C with the purpose of eliminating the humidity adsorbed by their components. Prior to recording the spectrum of a given sample, the background spectrum was obtained and automatically subtracted.

Spectra were recorded from 4000 to 450 cm^{-1}, the number of interferograms was fixed at 10 with a nominal resolution of 2 cm^{-1}, being the scan rate of 0.1 cm s^{-1}.

RESULTS AND DISCUSSION

Spectrum of AC

Spectrum of sample AC (Figure 1) shows several absorption bands between 4000 and 450 cm^{-1}, which are assigned as follows (11-13). The broad band centered at 3435 cm^{-1} is ascribed to stretching vibrations in hydroxyl groups, ν(OH). As the band is located at wave numbers lower than in the case of free OH groups, probably these groups are involved in hydrogen bonds (14). The weak band at 1720 cm^{-1} and the peak at 1632 cm^{-1} are connected with C=O bonds in different configurations (lactone, quetone, quinone, etc.). A number of bands of variable intensity located between 1600 and 1400 cm^{-1} have been associated with highly conjugated C=O groups in a quinone configuration (15-18), with aromatic ring stretching frequencies (19,20) whose intensity is enhanced by the presence of phenol or ether groups (21), with C⋯O type iono-radical structures (14), and with carboxilate anion (22,23). According to Zawadzki (11), the C⋯O structures are an intermediate stage in the process of formation of C=O groups (carboxyl) strongly bonded to the surface. The sharp peak situated at 1385 cm^{-1} can be assigned to the deformation vibrations of OH groups, δ (OH). In this spectral region also absorb radiation the CH_3 groups, but the presence in AC of surface methyl groups appears to be little probable as the material was first subjected to heat treatment at high temperatures in N_2 and then it remained in contact with an uncontrolled atmosphere until the oxidation treatments were effected. Therefore, adsorption upon AC of atmospheric oxygen and water likely occurred and this surface species, involved in hydrogen bonds, might be responsible for the spectral appearance of the band at 1385 cm^{-1}. This band usually presents variable intensity and, as a result, its practical utility in studies of structural assignments is limited (14,24). The several bands which overlap between 1300 and 950 cm^{-1} are attributed to ν (C-O) vibrations. In view of the high number of bands, the C-O bonds must be present in different oxygen functional groups and structures (namely, hydroxyl, ether, etc.). Finally, the weak bands displayed by the spectrum in the range 910-650 cm^{-1} are associated with out-of-plane deformations (for instance,

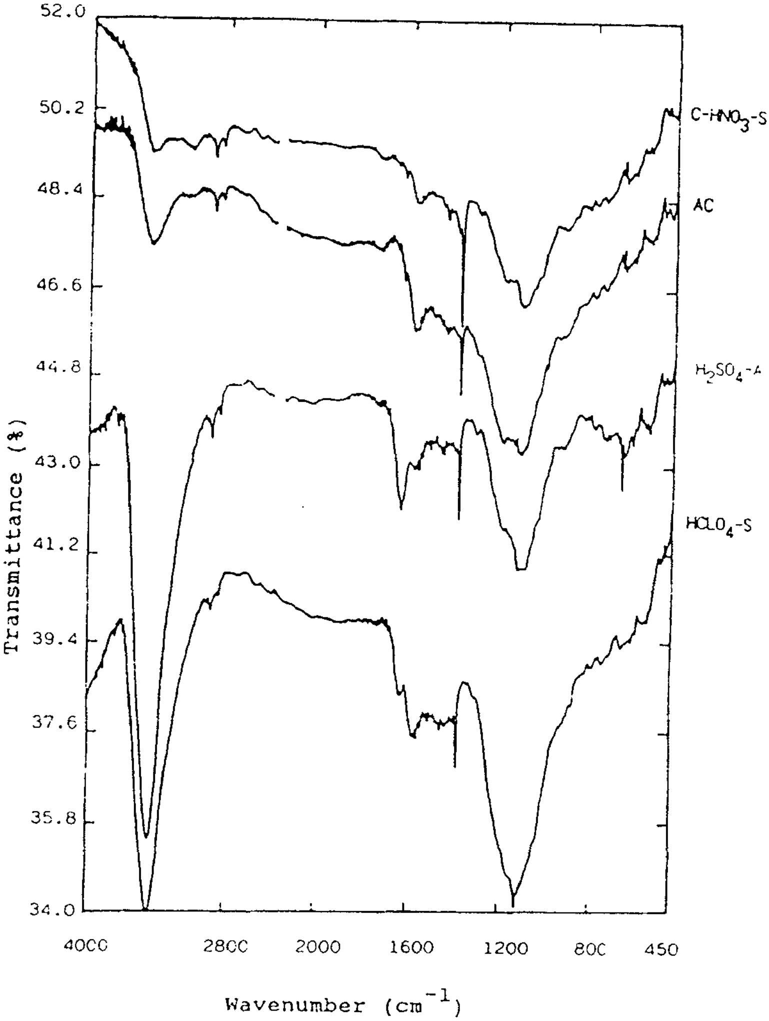

Figure 1.- FT-IR spectra of samples: AC, C-HNO_3-S, H_2SO_4-A and $HClO_4$.

in substituted benzenes) and CO_2 present in the path of the infrared radiation as well as with inorganic components of AC; in the assignment of these bands there is not a general agreement (24).

Influence of oxidizing agent.

Spectra of H_2SO_4 -A, C-HNO_3 -S and $HClO_4$ -S are shown in Figure 1. In comparison with the spectrum AC, in the spectra of H_2SO_4 -A and $HClO_4$ -S the bands at 3455 and 1630 cm^{-1} significantly increase their intensity. The band situated at 1630 cm^{-1} is weaker in the spectrum of $HClO_4$-S. Accordingly, the oxidation of AC with H_2SO_4 and $HClO_4$ leads to formation of OH and C=O groups to an extent which depends on the the oxidizing agent. In the case of H_2SO_4 -A, the increase in intensity of the band at 3435 cm^{-1} might be originated by surface H_2O (the oven-dried treatment effected on the pellets at 110°C before recording the FT-IR spectra might have partly affected the adsorbed species since it was carried out only for a short time), as this spectral feature is not accompanied by an increase in the intensity of bands between 1300 and 950 cm^{-1} indicative of ν (C-O) vibrations. Regarding $HClO_4$ -S, it is evident the enhanced presence of surface groups or structures containing C-O bonds. As for the spectrum of HNO_3, the band at 3435 cm^{-1} displays a different shape and some bands including the one at 1630 cm^{-1} decreases in intensity. The results obtained with H_2SO_4-A, $HClO_4$ -S and C-HNO_3-S differ from those previously reported (25), which were provided by the technique of thermogravimetric analysis. Between 35 and 800°C the DTG curves showed the occurrence of only one weight loss effect for H_2SO_4-A and $HClO_4$ -S and of two effects for C-HNO_3-S. This, in contrast to the spectral changes, suggested the presence of a larger number of different surface oxygen groups in C-HNO_3-S than in H_2SO_4-A and $HClO_4$ -S, which were absent from AC. Therefore, the thermally unstable groups either do not absorb energy between 4000 and 450 cm^{-1}, which seems to be little probable to occur, or the corresponding bands overlap with stronger bands due to groups which were unaffected by heating effect. In this connection it should be pointed out that the C-NO_2 vibrations give rise to bands at 1560 and 1360 cm^{-1} due to asy and sym stretchings, respectively (14). If so, both techniques provide us with a complementary information in this study on the surface chemistry of the samples of oxidized carbon. As at low temperatures H_2SO_4 (26) is a moderately good oxidizing agent and $HClO_4$ proves to be a relatively poor one due likely to the high kinetic energy barrier (26,27) and in view of the concentration of the solutions used (as inferred from Table 1, it was much higher for HNO_3 than for $HClO_4$ and H_2SO_4; in the case of HNO_3 it should be noted that its effectiveness as oxidizing agent was larger in a diluted solution, though dilution did not increase the surface C=O groups which absorb radiation at 1630 cm^{-1}, as seen below), which was consistent with the number and extent of formation of surface oxygen groups as inferred from the thermal analysis data (25), the spectroscopic results suggest that other factors markedly influence the oxidation of AC by these three mineral acids.

Spectra of H_2O_2-S, O_3-S, ClO_2-S, C-KIO_4-S and C-$KMnO_4$-S are shown in Figure 2. The spectra of H_2O_2-S, ClO_2-S and C-KIO_4-S display an increase in intensity of the bands at 3435 and 1385 cm^{-1}, which point out an enhanced presence in these samples of surface OH groups or adsorbed H_2O in comparison with AC (see Figure 1). Furthermore, in these three spectra the band located at 1630 cm^{-1} significantly increases in intensity, which is a proof indicating the formation of C=O groups. Moreover, the band at 1585 cm^{-1} almost disappears from the spectrum of ClO_2-S, whereas in the spectra of H_2O_2-S and C-KIO_4-S it gains a certain intensity. Therefore, the effect of oxidation on the atomic groupings absorbing radiation in this frequency range is dependent on the oxidizing agent used H_2O_2 or ClO_2 and KIO_4. Lastly, the broad band situated between 1300 and 950 cm^{-1} markedly decreases and increases in intensity, respectively, for ClO_2-S or H_2O_2-S and C-KIO_4-S. Accordingly, the groups or structures containing C-O bonds are affected in opposite directions depending on the oxidizing agent. In brief, H_2O_2, ClO_2 and KIO_4, similarly to H_2SO_4 and $HClO_4$, turn out to be effective agents in causing the oxidation of AC. Particularly, in the case of the ClO_2-S, as also happens mainly with C-HNO_3-S, the FT-IR results do not agree with those obtained by thermal analysis. Thus, the DTG curve of ClO_2-S did not present any pronounced maximum of weight loss in the temperature range 35-800°C. This fact even suggested us in accordance with the literature (2), a decrease in the oxidizing power of ClO_2 as a result of its rapid photodecomposition to a mixture of $HClO_3$ and HCl, being the first a weaker oxidizing agent than ClO_2. The FT-IR results, instead, suggest than the oxidation of AC with ClO_2 leads to formation of surface oxygen groups which are then thermally stable.

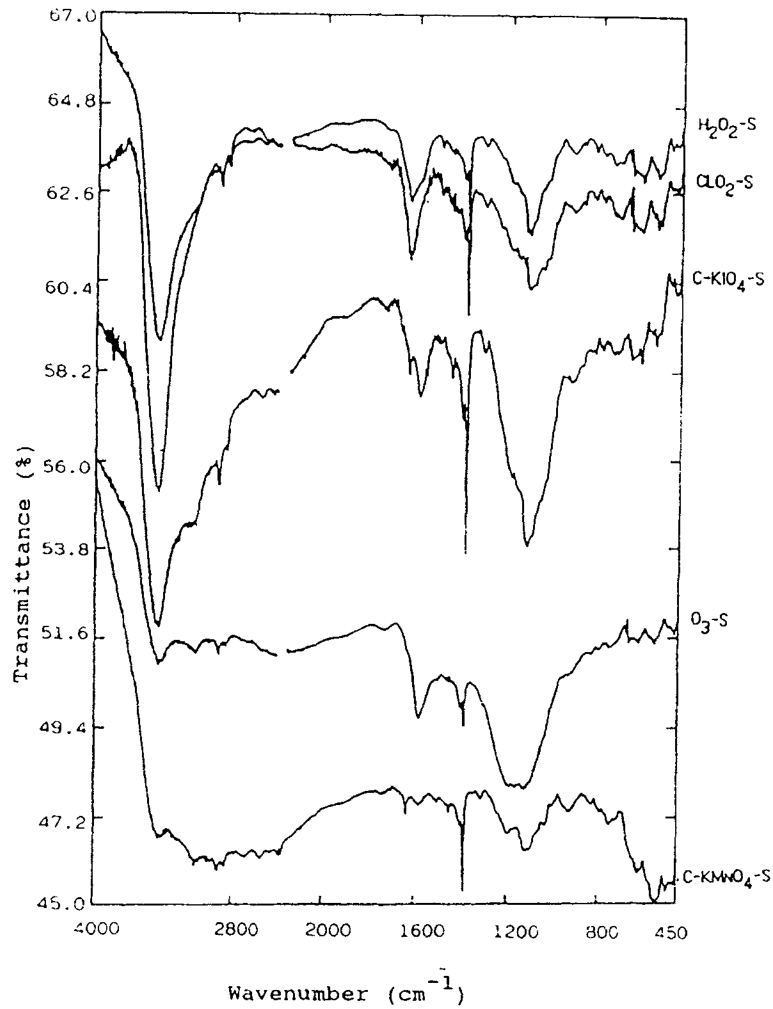

Figure 2.- FT-IR spectra of samples: H_2O_2-S, ClO_2-S, C-KIO_4-S, O_3-S and $KMnO_4$-S.

Apart from the dissimilar shape of the band at 3435 cm^{-1}, the only worth mentioning features in the spectrum of O_3-S (Figure 2) are the slight variations in intensity of the bands located at 1585 and 1120 cm^{-1}. Although this behaviour should be further investigated, it points at O_3-surface groups interactions which do not take place with the remaining oxidizing agents. In view of the strong oxidizing power of the O_3 in acid solution, as shown by the following values of the standard reduction potential:

$$O_3 + 2H^+ + 2e^- \rightleftarrows O_2 + 2H_2O \qquad E° = 2.070V \qquad [1]$$

$$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O \qquad E° = 1.776V \qquad [2]$$

$$ClO_3 + H^+ + 1e^- \rightleftarrows HClO_2 \qquad E° = 1.270V \qquad [3]$$

$$H_5IO_6 + H^+ + 2e^- \rightleftarrows IO_3^- + 3HO_2 \qquad E° = 1.601V \qquad [4]$$

it appears striking the behaviour shown by O_3. Perhaps, it is connected with the concentration or pH, or with both, of the O_3 solution. The low concentration of the ozone solution was due not only to the ratio O_3/ O_2 used but also the O_3 solubility in water.

The spectrum of C-$KMnO_4$-S (Figure 2) shows a generalized poor development of most absorption bands in comparison with the spectrum of AC (Figure 1). The scanty presence of surface oxygen groups in C-$KMnO_4$-S suggests that at the solution pH, which is a weakly acid pH, MnO_4^- first interacts with surface groups of AC and reduces to Mn^{2+} according to reaction [5]:

$$MnO_4^- + 8\,H^+ + 5\,e^- \rightleftarrows Mn^{2+} + 4\,H_2O \qquad E°= 1.491\ V \qquad [5]$$

and then Mn^{2+} oxidizes by excess MnO_4^- to MnO_2 by reaction [6]:

$$2\,MnO_4^- + 3\,Mn^{2+} + 2\,H_2O \rightleftarrows 5\,MnO_2 + 4\,H^+ \qquad [6]$$

Evidences on the formation of MnO_2 by reaction [6] comes from the ash content for C-$KMnO_4$-S which is much higher than for AC and the samples prepared using other oxidizing agents (as a guiding example, the ash content was 3.22% for C-KIO_4-S and 19.72% for C-$KMnO_4$-S), and by the increase in absorption between 800 and 450 cm^{-1} in its FT-IR spectrum. Also, it was by the results of the thermogravimetric analysis (25), as in the case of C-$KMnO_4$-S there was an effect of weight loss centered at 530°C which was connected with the thermal decomposition of MnO_2 by reaction [7]:

$$4\,MnO_2 \rightleftarrows 2Mn_2O_3 + O_2 \qquad [7]$$

Despite the formation of MnO_2 and, as a result, the oxidizing action of $KMnO_4$ the spectrum of C-$KMnO_4$-S does not show any feature which reveals the presence in this sample of the surface oxygen groups arising from the redox reaction involving MnO_4^-, which is really a surprising result.

Influence of pH

The main spectral changes in the spectra of H_2O_2-A and H_2O_2-B (Figure 3) compared with the spectrum of AC (Figure 1) concern the band at 3435 cm^{-1} and bands between 1300 and 950 cm^{-1}, which greatly increase in intensity. This denotes formation of OH groups and also, perhaps, of ether type structures. Despite the presence of H_2SO_4 in the H_2O_2 solution used in preparation of H_2O_2-A, C=O groups are not formed. Allowing for the results obtained with H_2O_2-S, it follows that the oxidation of AC yields a different surface chemistry only when the oxidizing treatment of the material was effected using the H_2O_2 solution at unchanged pH. Variations in the oxidizing action of H_2O_2 by effect of pH changes were expected since, according to the literature (26), when H_2O_2 in aqueous solution act as an oxidizing agent the mechanisms and the products of the reactions are very sensitive to pH, and at basic pH they use to be faster than at acid pH. However, the behaviour shown by H_2O_2 at acid and basic pH is not consistent with the values of the standard reduction potential for the reduction reactions of H_2O_2 in both media:

$$(a_{H^+} = 1) \quad H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O \quad E^\circ = 1.776V \qquad [8]$$

$$(a_{OH^-} = 1) \quad HO_2^- + H_2O + 2e^- \rightleftarrows 3OH^- \quad E^\circ = 0.870V \qquad [9]$$

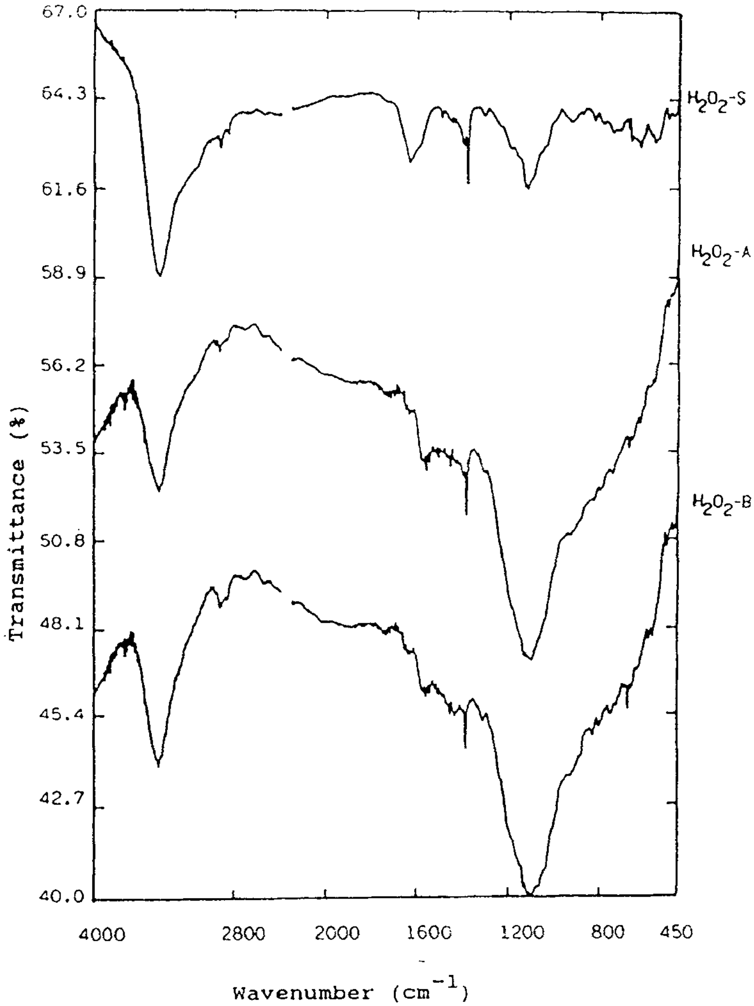

Figure 3.- FT-IR spectra of samples oxidized with H_2O_2 at different pH.

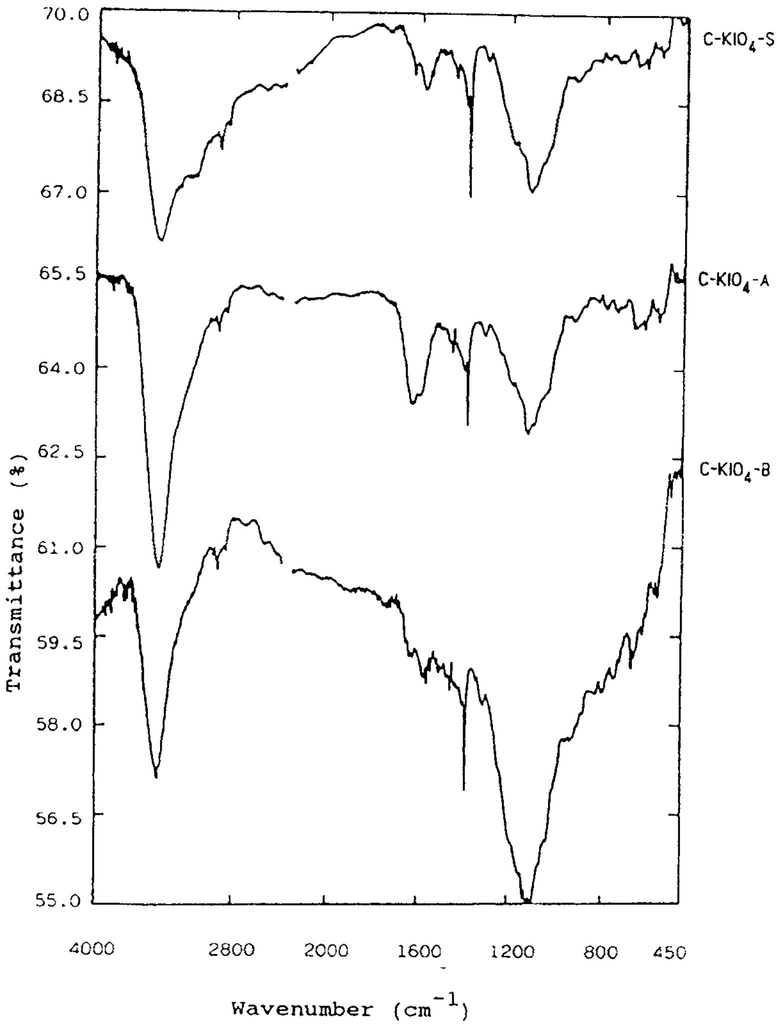

Figure 4.- FT-IR spectra of samples oxidized with KIO_4 at different pH.

since H_2O_2 in the solution at acid pH should be a stronger oxidizing agent than in the solution at basic pH. In this connection it should be pointed out that the results of the thermogravimetric analysis indicated the existence of a strong effect of weight loss centered at 264°C in the heat treatment of H_2O_2-A only, which was in good agreement with variation in the oxidizing power by pH change in the H_2O_2 solution. The similar behaviour shown by H_2O_2 in both media in the present study might be connected with the surface groups present in AC when the H_2O_2 solutions were brought into contact with the material. When in aside experiments AC was outgassed at 250°C for 2 h prior to its oxidation, this was then pH dependent and accordingly the chemical nature and the extent of formation of the surface oxygen groups were influenced by pH (28).

As shown the spectra of C-KIO_4-A, C-KIO_4-S and C-KIO_4-B (Figure 4) compared with the spectrum of AC (Figure 1), the surface chemistry which emerges from the oxidation of AC using KIO_4 solutions at three different pH values is greatly influenced by pH. At acid pH surface groups, which absorb radiation at 1630 cm^{-1} and at wave numbers close to 1600 cm^{-1}, are formed to a large extent, which further is similar. Groups and structures containing C-O bonds, instead, disappear significantly from the surface of the oxidized material. At basic pH it decreases the presence of surface of groups and C-O-C structures. Accordingly, KIO_4 in a solution at acid pH is a stronger oxidizing agent than in the solution at basic pH, which agrees with the values of the standard reduction potentials for reactions [10] and [11]:

$$a_{H^+} = 1 \qquad H_5IO_6 + H^+ + 2e^- \rightleftarrows IO_3^- + 3H_2O \qquad E^\circ = 1.601\ V \qquad [10]$$

$$a_{OH^-} = 1 \qquad H_3IO_6^{2-} + 2e^- \rightleftarrows IO_3^- + 3HO^- \qquad E^\circ = 0.700V \qquad [11]$$

The spectra of C-$KMnO_4$-S and C-$KMnO_4$-B (Figure 5) show a very marked increase in intensity of the bands located at 3435 and 1630 cm^{-1} which points at the formation of OH and C=O groups at both pH values. (As the increased intensity of the band at 3435 cm^{-1} in the spectrum of C-$KMnO_4$-A is not parallel in the bands between 1300 and 950 cm^{-1}, probably the former spectral feature is associated with the update of H_2O by the carbon during its contact with $KMnO_4$ solution). As the

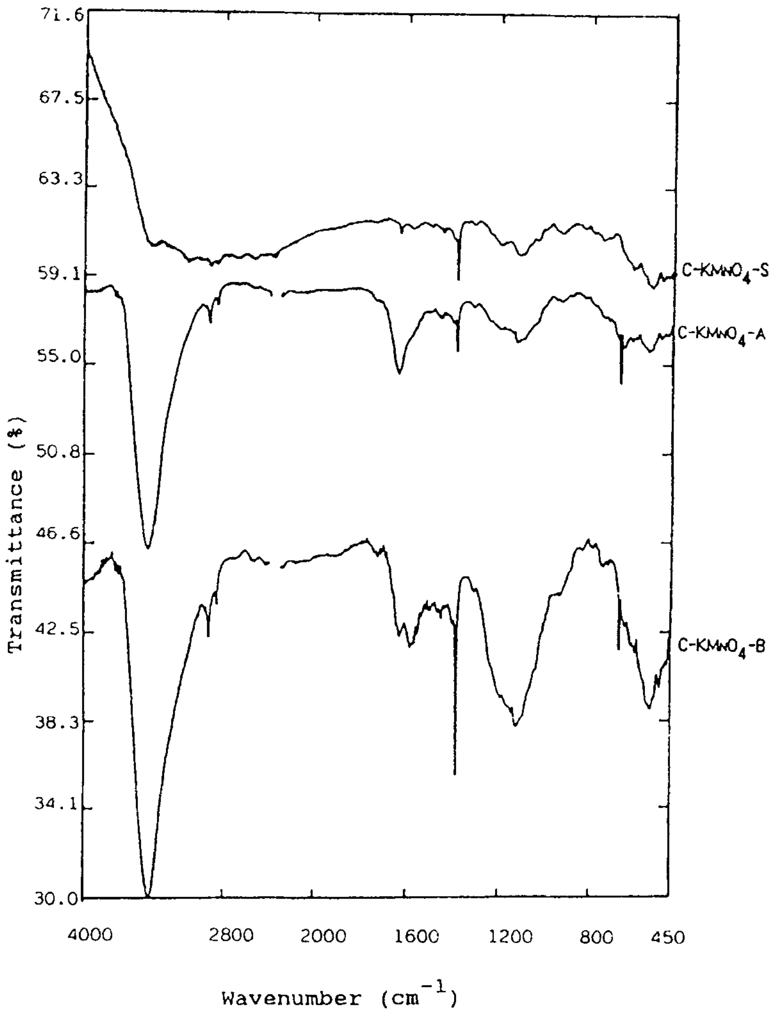

Figure 5.- FT-IR spectra of samples oxidized with $KMnO_4$ at different pH.

increase in intensity of the band at 1630 cm^{-1} is similar in the spectra of the ClO_2-S, H_2O_2-S and KIO_4-A, the oxidation of AC with the distinct oxidizing agents results in the formation of a close amount of C=O groups, though it depends not only on the oxidizing agent but also on pH of the solution. In the spectrum of $KMnO_4$-B also develops the band situated at 1585 cm^{-1}, which points at the formation of the atomic groupings which absorb radiation in this range of wave numbers. $KMnO_4$ acting as oxidizing agent in acid solutions should be stronger than in alkaline solutions, as shown by the values of the standard reduction potentials for reactions [12] and [13]:

$$a_{H+} = 1 \quad MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O \qquad E^\circ = 1.491\ V \qquad [12]$$

$$a_{OH-} = 1 \quad MnO_4^- + 2H_2O + 3e^- \rightleftarrows MnO_2 + 4OH^- \qquad E^\circ = 0.558\ V \qquad [13]$$

Finally, it is worth mentioning that especially in the spectrum of C-$KMnO_4$-B the absorption greatly increases at wave numbers lower than 800 cm^{-1}, which is consistent with a large formation of MnO_2 by reaction [13]. MnO_2 might have a negative influence on the oxidation of AC by prevention of mass transport in AC porosity. In addition, as MnO_2 is insoluble in water and thus it was not removed by the washing treatment effected periodically on C-$KMnO_4$-S after the oxidation of AC, it might affect the FT-IR results by causing changes in the mass of sample used to obtain the spectra.

Influence of concentration

As in the spectrum of C-HNO_3-S the bands located at 1585 cm^{-1} and between 1300 and 950 cm^{-1} are weaker than in the spectrum of D-HNO_3-S (Figure 6), the surface groups or structures which are responsible for their spectral appearance are present to a larger extent in the latter sample. Then, the increase in concentration of the HNO_3 solution has a negative influence on the oxidation of AC. This may be connected with a more disordered entrance of the oxidizing agent in AC porosity in the case of the concentrated solution and, as a result, with the lesser degree of interaction of HNO_3 with AC than when the relatively dilute solution is used. In fact, in the spectrum of C-HNO_3-S even some bands, as the one located at 1630 cm^{-1}, display a decreased intensity with regard to the spectrum of AC (Figure 1).

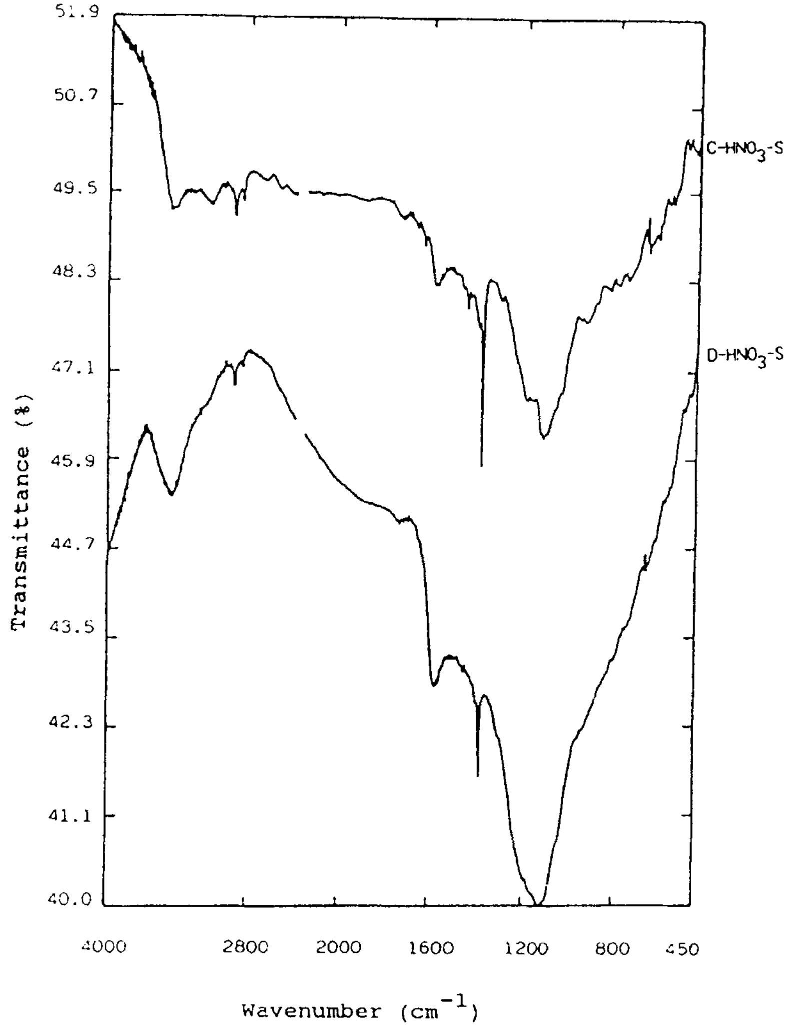

Figure 6.- FT-IR spectra of samples oxidized with HNO_3 varying the concentration.

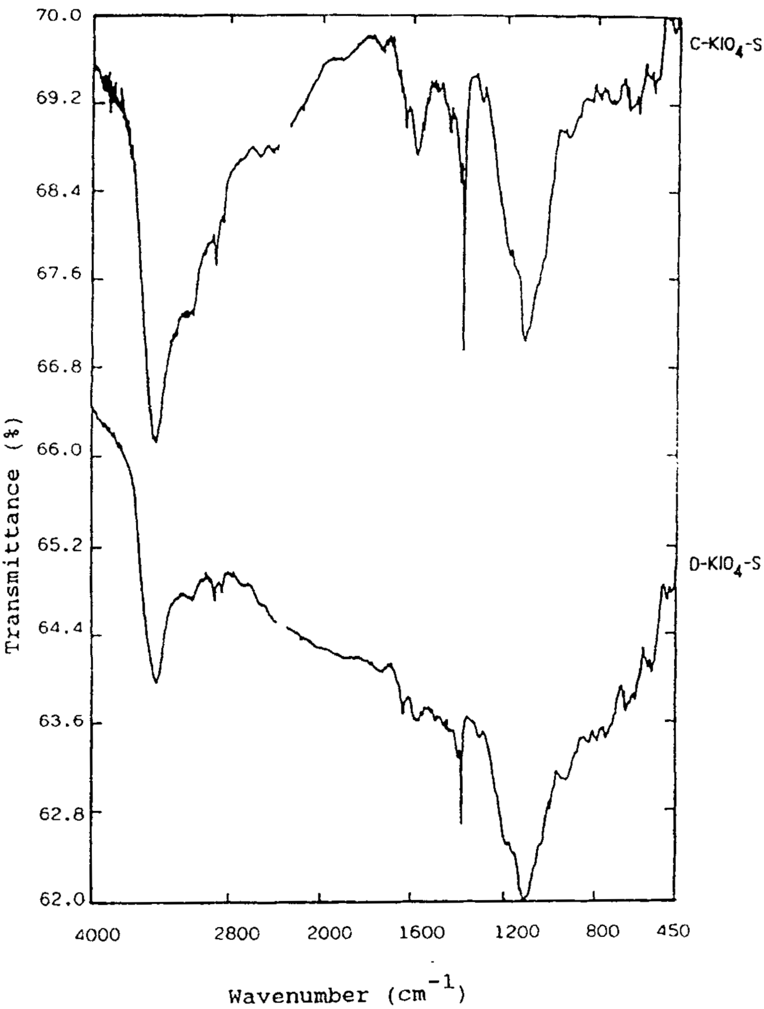

Figure 7.- FT-IR spectra of samples oxidized with KIO_4 varying the concentration.

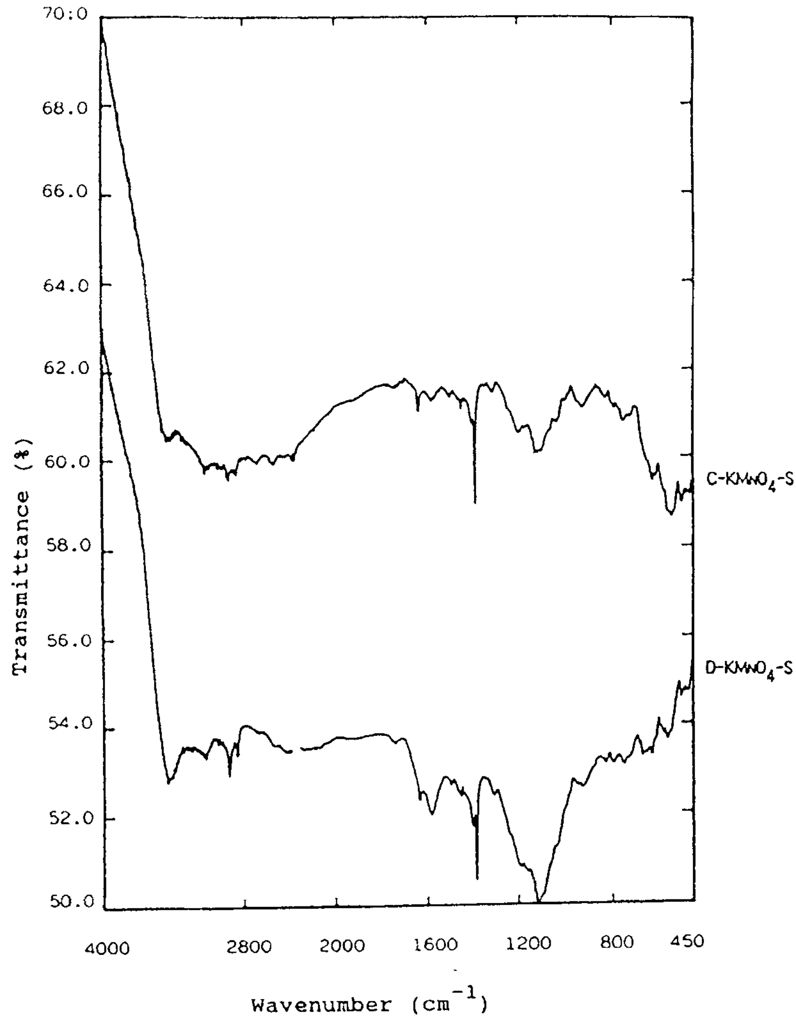

Figure 8.- FT-IR spectra of samples oxidized with $KMnO_4$ varying the concentration.

However, in the case of D-KIO_4-S and C-KIO_4-S (see Figure 7), the presence of surface (OH, C=O, C-O-C, etc.) groups is more accused in the sample prepared using the KIO_4 concentrated solution. Accordingly, the oxidation of AC by KIO_4 is favoured with the increase in concentration of the KIO_4 solution. As for $KMnO_4$, from the intensity of the band at 1630 cm^{-1} in the spectrum of D-$KMnO_4$-S (figure 8) compared with the spectra of AC and C-$KMnO_4$-C it follows that with this oxidizing agent also surface C=O groups are formed when the oxidation of AC is performed with the dilute solution. Therefore, important differences are noted in the behaviour of mainly HNO_3 or $KMnO_4$ and KIO_4.

From the above results on the oxidation of AC using different oxidizing agents in solutions of varying pH and concentration, together with previous results provided by the technique of thermogravimetric analysis, it can be deduced that, generally, the expected oxidizing power for the chemicals used is not the only factor which influences the oxidation of the material. A more or less ordered entrance of the oxidizing agent in AC pores depending on concentration of the solution and on interactions occurring in the solution with participation of solvent molecules, the diffusion of the oxidizing agent in AC porosity which will be influenced by the molecular size of species involved, the ease of interaction of the oxidizing agent with surface oxygen groups already present in AC on effecting the oxidation treatment, and the formation in redox processes of insoluble products with prevention effect on mass transport might be responsible for the differences shown by the oxidizing agents towards the oxidation of AC.

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