

# Decomposition of H<sub>2</sub>O<sub>2</sub> on activated carbon obtained from olive stones

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**Abstract:** Activated carbons were prepared from olive oil solid wastes by treatment in different schemes: impregnation with H<sub>3</sub>PO<sub>4</sub> followed by pyrolysis at 300–700 °C, by steam pyrolysis at 600–700 °C, or by conventional steam activation at 850 °C. Porosity characteristics were determined by analysis of nitrogen adsorption isotherms, and carbons of widely different properties and surface pH values were obtained. Decomposition of H<sub>2</sub>O<sub>2</sub> in dilute unbuffered solution was followed by measuring evolved oxygen volumetrically. First-order kinetics was followed, and the catalytic rate coefficients were evaluated. The carbons tested showed appreciable activity where evolved oxygen attained ≈10% of the stoichiometric amount in 1 h. The degree of decomposition showed inverse dependence on surface area, pore volume and mean pore dimensions. The chemical nature of the surface, rather than the porosity characteristics, was the principal factor in enhancing the disproportionation of H<sub>2</sub>O<sub>2</sub> on the activated carbon surface.

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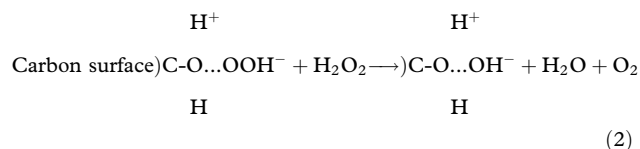
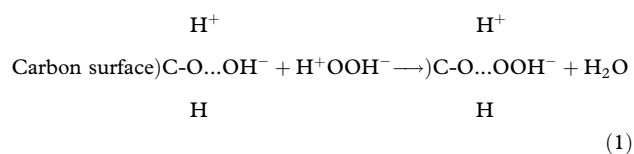
**Keywords:** activated carbon; H<sub>2</sub>O<sub>2</sub> decomposition; porosity; surface acidity

## INTRODUCTION

Activated carbons are well distinguished universal and versatile adsorbents for a large number of organic and inorganic species, both from the liquid and gas phases. They derive their outstanding properties from the extended surface area and their porosity. Such properties are a function of both the precursor and scheme of preparation (and/or activation). These not only determine their porosity but also the chemical nature of their surfaces, which consequently establishes their adsorptive as well as catalytic characteristics.<sup>1</sup> It is now accepted that the acid or base character of a carbon is developed according to the history of its formation and the temperature at which it was oxidized. The low-temperature activated carbons have been found to develop acidic surface functional groups (phenolic, carboxylic, lactonic, cyclic peroxides, and carbonyl groups), which are hydrophilic in character. These are the L or acidic carbons, which preferentially adsorb alkalis. Carbons activated at higher temperatures (800–1000 °C) develop basic oxides (eg chromene and pyrone-like structures). These are the H- or basic-type carbons, which adsorb mineral acids but little alkali.<sup>1,2</sup> The nature and amount of complexes formed with the surface oxygen are affected by the surface area, particle size and ash content, as well as the degree of carbonization/gasification.<sup>3</sup>

Carbon materials have also been used for a long time in heterogeneous catalysis, because they act as either direct catalysts or, more important, they can satisfy most of the desirable properties required for a suitable support. Charcoals and activated carbon have been

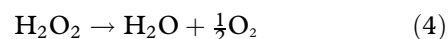
shown to exhibit catalytic activity in the decomposition of hydrogen peroxide. Different factors have been postulated to be effective in this reaction,<sup>1</sup> these are: H<sub>2</sub>O<sub>2</sub> concentration, temperature, nature of the carbon surface, carbon surface area, surface and medium pH, and surface treatment. It has been assumed that<sup>1</sup> decomposition of H<sub>2</sub>O<sub>2</sub> by activated carbon involves primary exchange of an oxonium-hydroxyl group with a hydrogen peroxide anion. The adsorbed peroxide was regarded as having an increased oxidation potential and thus decomposed another H<sub>2</sub>O<sub>2</sub> molecule, with release of O<sub>2</sub> and regeneration of the carbon.



Decomposition of H<sub>2</sub>O<sub>2</sub> was, meanwhile, thought to proceed through its dissociation as a weak acid:



and not through the reaction



The OOH<sup>-</sup> anion, being even less stable than the

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H<sub>2</sub>O<sub>2</sub> itself, decomposed very readily. These assumptions predict that in an alkaline medium the dissociation of H<sub>2</sub>O<sub>2</sub> will be enhanced, whereas it will be suppressed in the acidic medium. These conditions will be favoured either in the solution or on the carbon surface which determines the catalytic decomposition reaction.

Although the nature of the carbon surface and existing acidic/basic sites play a critical role, in some cases the extent of the carbon surface was reported to be effective.<sup>1</sup> On carbons with a relatively higher surface area the catalytic sites will be widely distributed in such a manner as to enhance decomposition, whereas when densely distributed an inhibiting action may prevail. When the catalytic reaction was carried out in a buffer solution using different carbon blacks, the catalytic activity was related to surface area.<sup>1,3</sup>

Most of the earlier investigations were essentially concerned with the factors and conditions affecting the rate and extent of H<sub>2</sub>O<sub>2</sub> decomposition catalysed by activated carbons.<sup>1,4-14</sup> More recent studies were directed towards applying this type of reaction for practical purposes, especially in problems related to environmental impacts.<sup>15-22</sup> One of these studies deals with the treatment of water effluents contaminated with H<sub>2</sub>O<sub>2</sub> which are usually generated from semiconductor manufacture, paper-making and many other processes.<sup>16,17,19</sup> This carbon-catalysed reaction is not only utilized in the decontamination of H<sub>2</sub>O<sub>2</sub>-loaded waters, but also finds other applications in the oxidative degradation of organics (eg humic acids, phenols, chloramines) as well as inorganic substances (such as H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>2</sub>, peroxides) in water effluents.

The advantage of activated carbon in this process is that it has a granular structure with a high surface area, so that fixed bed reactors can be used. The catalytic activity of activated carbon was assumed to be a result of the graphitic structures of the carbon, as well as of its surface functionalities. Recently, Lucking *et al*<sup>22</sup> reported the catalytic role of various activated carbons, in comparison with iron powder or graphite, in acting as heterogeneous catalysts for the activation of H<sub>2</sub>O<sub>2</sub> and the oxidation of 4-chlorophenol. It was confirmed

that activated carbons, from different sources and with high surface areas, showed appreciable catalytic decomposition of dilute H<sub>2</sub>O<sub>2</sub> solutions buffered at pH 3 and free from 4-chlorophenol. A carbon impregnated with 15% iron hydroxide showed a rather lower extent of decomposition than its precursor counterpart. The amount of iron found in the aqueous solution after 4h of reaction was less than 0.5 mg dm<sup>-3</sup> for all activated carbons used (including the impregnated carbon). Due to this low concentration of iron ions, the participation of a homogeneous reaction in the decomposition of H<sub>2</sub>O<sub>2</sub> can be excluded. Meanwhile, the decomposition proceeded considerably more slowly when a well-known activated carbon, F-300 (chemiron), was used. It was concluded that the extent and rate of decomposition depend on the nature of the activated carbons used. The present investigation reports the decomposition of H<sub>2</sub>O<sub>2</sub>, in unbuffered aqueous solutions, by activated carbons derived from olive oil mill wastes. Twelve carbons were prepared under various conditions of activation, such that a set of products was obtained, from same precursor, with varying textural and surface-chemical characteristics. The objectives were to demonstrate the role of: (i) scheme of activation, (ii) porous structure, and (iii) surface pH, on the kinetics of H<sub>2</sub>O<sub>2</sub> decomposition. Correlations between these factors and the disproportionation of H<sub>2</sub>O<sub>2</sub> are examined.

## MATERIALS AND TECHNIQUES

### Materials

Twelve activated carbons (AC) were prepared from dried crushed discard olive stone cake. Seven carbons were obtained by impregnation with H<sub>3</sub>PO<sub>4</sub> (30–70%) followed by thermal treatment at 300, 500 or 700 °C (Table 1). Two carbons were obtained by the more recently developed single-step steam pyrolysis<sup>23</sup> at 600 and 700 °C, two by the conventional thermal activation at 850 °C by either steam/N<sub>2</sub> or steam/CO<sub>2</sub>, and one carbon by preimpregnation with NH<sub>4</sub>Cl<sup>24</sup> followed by carbonization at 600 °C.

The activated carbons were characterized by N<sub>2</sub>/

**Table 1.** Description of activated carbons and their respective porosity characteristics

Activant	HTT (°C)	Notation	S <sup>z</sup> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>n</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>meso</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>o</sub> (cm <sup>3</sup> g <sup>-1</sup> )	r (nm)
30% H <sub>3</sub> PO <sub>4</sub>	300	P-33	310	158	0.335	0.218	0.061	2.45
30% H <sub>3</sub> PO <sub>4</sub>	500	P-35	422	161	0.389	0.241	0.117	1.88
30% H <sub>3</sub> PO <sub>4</sub>	700	P-37	408	248	0.382	0.241	0.096	1.79
50% H <sub>3</sub> PO <sub>4</sub>	500	P-55	675	249	0.475	0.223	0.182	1.46
60% H <sub>3</sub> PO <sub>4</sub>	500	P-65	750	263	0.542	0.257	0.173	1.51
70% H <sub>3</sub> PO <sub>4</sub>	500	P-75	506	278	0.467	0.272	0.117	1.82
50% H <sub>3</sub> PO <sub>4</sub>	700	P-57	598	214	0.498	0.288	0.142	1.87
Steam Py	600	S600	171	59	0.109	0.068	0.040	1.30
Steam Py	700	S700	270	56	0.227	0.105	0.121	1.73
Steam/N <sub>2</sub>	850	SN	90	23	0.056	0.024	0.026	1.12
Steam/CO <sub>2</sub>	850	Sd	113	62	0.103	0.061	0.021	1.77
NH <sub>4</sub> Cl	600	NH <sub>4</sub> Cl	199	14	0.095	0.026	0.065	0.95

77K, and the isotherms analysed by application of the  $\alpha_s$ -method.<sup>25</sup> Several textural parameters were evaluated:  $S^z$  (total specific surface area),  $S_n^z$  (non-microporous area), total pore volume,  $V_p$  (amount adsorbed at a relative pressure of  $p/p^0=0.95$ ), micropore volume,  $V_o^z$ , and mesopore volume,  $V_{meso}$  (from volume at  $p/p^0=0.10-0.95$ ).<sup>26</sup> An estimate for the mean pore radius was calculated by  $r=2V_p/S^z$ . The pH of the carbons was determined by measuring the suspension of fine carbon in distilled water (preboiled for 2 min and then cooled).

### Techniques

Decomposition of  $H_2O_2$  ( $0.80 \text{ mol dm}^{-3}$ ) was determined by kinetically following the evolution of oxygen during the reaction. The assembly employed is composed of a double-wall Pyrex glass cell ( $100 \text{ cm}^3$ ) fitted with a Quickfit two-way connection. One connection is for round-bottom ( $50 \text{ cm}^3$ ) flask containing  $H_2O_2$  solution, which could be tilted so as to be poured into the reaction vessel at the start of reaction. The second connection is an outlet for the produced oxygen attached to a glass manometer through a flexible hose to a graduated burette.

In each experiment 20 mg of the predried pulverized AC powder ( $\leq 100$  mesh) were added to the reaction cell containing  $10 \text{ cm}^3$  of distilled water, then mounted on a magnetic stirrer and connected to the two-way attachment. The side round-bottom flask was charged with  $2 \text{ cm}^3$  of fresh  $0.8 \text{ mol dm}^{-3} H_2O_2$  and  $10 \text{ cm}^3$  of distilled water, and connected by the side Quickfit joint to the reaction cell. Thermostatted water at  $30^\circ\text{C}$  was pumped through the glass jacket of the cell and stirring started so as to mix the suspension of AC to ensure good dispersion. Diluted  $H_2O_2$  in the round-bottom flask was then poured into the AC suspension, when  $30^\circ\text{C}$  was attained, and time recorded. The liquid level inside the gas manometer was adjusted to the atmosphere and the volumes recorded. Readings were determined at increasing time intervals (0.5 min, 1 min, then 5 min beyond 20 min) up to 1 h of reaction.

All experiments were repeated twice so that the data obtained are the mean of two determinations.

## EXPERIMENTAL RESULTS

### General considerations

Decomposition of  $H_2O_2$  on the tested activated carbons may be ascribed to both of their physico-chemical characteristics (porosity and/or surface chemical nature) or to the contaminating ash. However, the concentration of metals, eg iron, manganese and copper in plant materials lies within 10–50 ppm in the dry matter, which applies to the olive mill wastes employed in this investigation.<sup>27</sup> One experiment was carried out to detect the possible role of incorporated ash, by igniting an AC (S600) at  $900^\circ\text{C}$  followed by determining its catalytic activity, which proved to show no detectable action. The same carbon sample (S600) was washed by HCl, to get rid of soluble oxide; its activity decreased to some extent (volume at  $1 \text{ h}=11.0 \text{ cm}^3$ ) as compared with the corresponding non-treated activated carbon ( $12.90 \text{ cm}^3$ ). This could be due to increased surface acidity adversely affecting the reaction, and proves that the principal constituent responsible for the catalytic disproportionation of  $H_2O_2$  would be the activated carbon itself.

Since the decomposition of  $H_2O_2$  was postulated to be affected by the medium (or surface) pH, the present results were confined to non-buffered solutions to investigate the influence of the inherent carbon acidity–basicity. The pH values of slurries of the tested carbons were observed to vary considerably between 4.9 and 9.5 (Table 2).

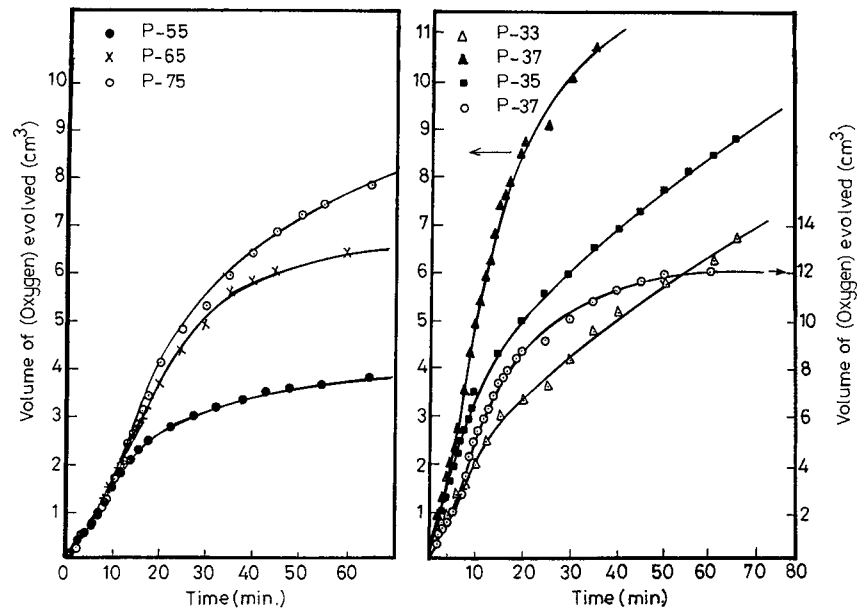
It should be noted that the tested carbons display, in addition, a wide range of porosity characteristics (surface area =  $90-750 \text{ m}^2 \text{ g}^{-1}$ , pore volume =  $0.056-0.542 \text{ g}^{-1}$ , and average pore radius =  $0.95-2.45 \text{ nm}$ ).

### Efficiency of the various activated carbons in decomposing $H_2O_2$

Figures 1 and 2 demonstrate the kinetic oxygen evolution curves, and show short induction periods

**Table 2.** Kinetic parameters for the decomposition of  $H_2O_2$  on different activated carbons ( $C_o=0.802 \text{ mol dm}^{-3}$ , carbon dose =  $909 \text{ mg dm}^{-3}$ ,  $2 \text{ cm}^3$  (30 vol%)  $H_2O_2+20 \text{ cm}^3 H_2O+20 \text{ mg AC}$ )

Sample	pH	$k \times 10^{-3} (\text{min}^{-1})$	Vol at 1h ( $\text{cm}^3$ )	% decomp (1h)	Carbon dose (mg)	$V(O)/S^z \times 10^2 (\text{cm}^3 \text{ m}^{-2})$
P-33	5.7	1.05	6.30	3.2	616	2.03
P-35	5.5	1.75	8.25	4.2	470	1.95
P-37	5.2	2.49	12.00	6.2	323	2.94
P-55	5.1	0.81	3.70	1.9	1048	0.55
P-65	5.4	0.85	6.35	3.3	611	0.84
P-75	5.0	0.85	7.75	4.0	501	1.53
P-57	4.9	1.55	4.70	2.4	825	0.78
S600	7.6	3.30	12.90	6.6	301	7.54
S700	7.7	3.46	15.20	7.8	255	5.63
SN	8.1	2.51	13.90	7.1	279	15.44
Sd	8.7	3.35	15.20	7.8	255	13.45
NH <sub>4</sub> Cl	9.5	3.60	18.10	9.3	214	9.09



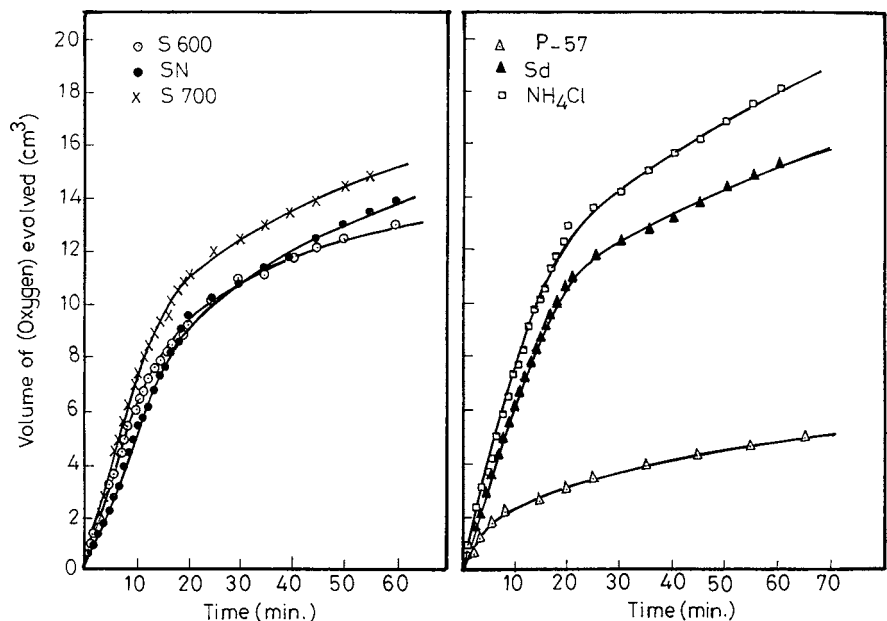
**Figure 1.** Kinetic decomposition of  $H_2O_2$  on some activated carbons (for notation refer to Table 1).

(1–5 min) as well as high slopes at and beyond 1 h of contact. This might be ascribed to diffusion resistance through the internal micropores, as well as to reaction on sites of different activities. First-order kinetic law was found to apply with satisfactory linearization up to contact periods of 10–20 min (Figs 3 and 4).

Many kinetic parameters were estimated for each activated carbon; these are (1) the specific rate constant ( $k$ ,  $\text{min}^{-1}$ ) from slopes of the plots of  $\ln V_s / (V_s - V_t)$  vs  $t$  ( $V_s$  = stoichiometric volume of oxygen evolved according to eqn (4),  $V_t$  = volume of oxygen evolved up to time  $t$ ), (2) volume of oxygen evolved up to 60 min, (3) percent decomposition at  $t = 60$  min (% dec =  $V_t / V_s \times 100$ ), and (4) weight of AC necessary to release the stoichiometric volume of oxygen (carbon dose in mg), under the conditions of the experiment. The results are given in Table 2. These four par-

ameters are considered to describe properly the catalytic decomposition at the initial stage (10–20 min) as well as during the decay period.

It appears, generally, that the present carbons catalyse the disproportionation reaction of  $H_2O_2$  to an appreciable extent. Measurable amounts of oxygen gas are evolved ( $3.7\text{--}18.1\text{ cm}^3\text{ h}^{-1}$ ) which indicate decompositions of 2.0–9.3% of the  $H_2O_2$  present in solution. The carbon dose, shown in Table 2, also confirms the diversity of activity in a distinct manner, as it varies between 214 and 1048 mg. Moreover, varying initial rate constants are observed ( $0.85\text{--}3.6\text{ min}^{-1}$ ) that are almost linearly related to the activity at 1 h (Fig 5). These differences could be associated with individual differences in the characteristics of the carbon, or to the conditions of preparation.



**Figure 2.** Kinetic decomposition of  $H_2O_2$  on some activated carbons.

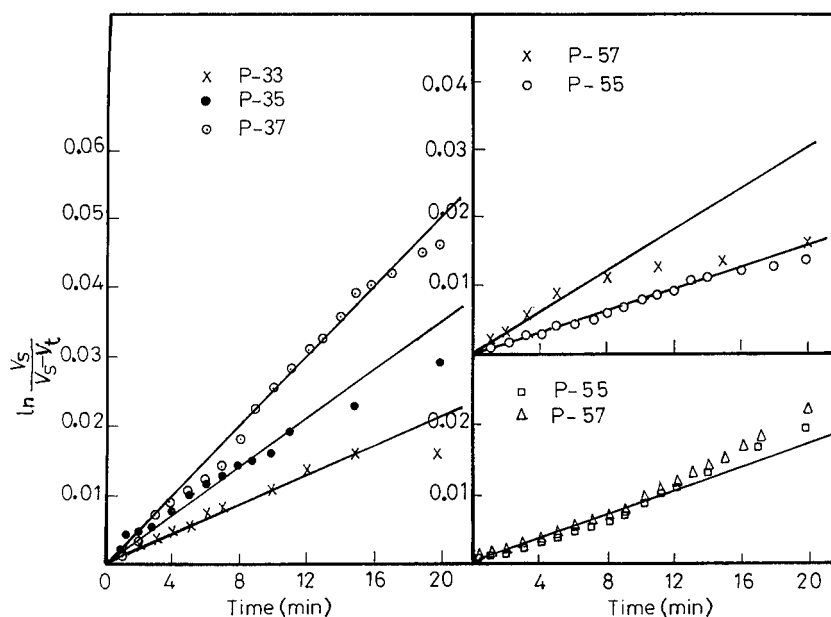


Figure 3. First order plots for decomposition of H<sub>2</sub>O<sub>2</sub> on activated carbon.

### Dependence of catalytic decomposition on carbon porosity

Since the catalytic decomposition is a surface reaction, the available surface and extent of porosity are expected to play an important role. Figure 6 displays the correlation between volume of oxygen evolved after 1 h and three textural parameters ( $S^z$ ,  $V_p$  and  $r$ ). It is astonishing to notice that, apparently, the extent of decomposition is an inverse function of the three porosity characteristics. It also shows inverse proportionality to other textural parameters (Fig 7), namely the external, or non-porous surface area ( $S_n$ ), the volume within mesopores ( $V_{meso}$ ) and the volume inside the micropores ( $V_{mic}$ ). This suggests that the limiting decomposition (after 1 h) is not a function of any of the porosity characteristics. Extended surface areas (or large pore volumes), or wider pores, do not

enhance decomposition but rather reduce it and the results suggest that the catalytic action of the present carbons is influenced by either the conditions of preparation, or the chemical nature of the surface.

### Dependence of catalytic decomposition on surface acidity and conditions of preparation

Upon considering the data in Table 2 and Figs 1–4 and 8, it appears that the tested carbons show two distinct groups with respect to their catalytic activity. The first group (I) are acidic and low to moderately active, whereas the second (II) are basic and distinctly better decomposers for H<sub>2</sub>O<sub>2</sub> as evidenced by both  $k$  and  $V(O)$  values (Table 2 and Fig 8). The second group (II) are, meanwhile, characterized by low surface areas ( $S^z=90-270\text{m}^2\text{g}^{-1}$ ) and low pore volumes ( $V_p=0.056-0.227\text{cm}^3\text{g}^{-1}$ ) as compared with

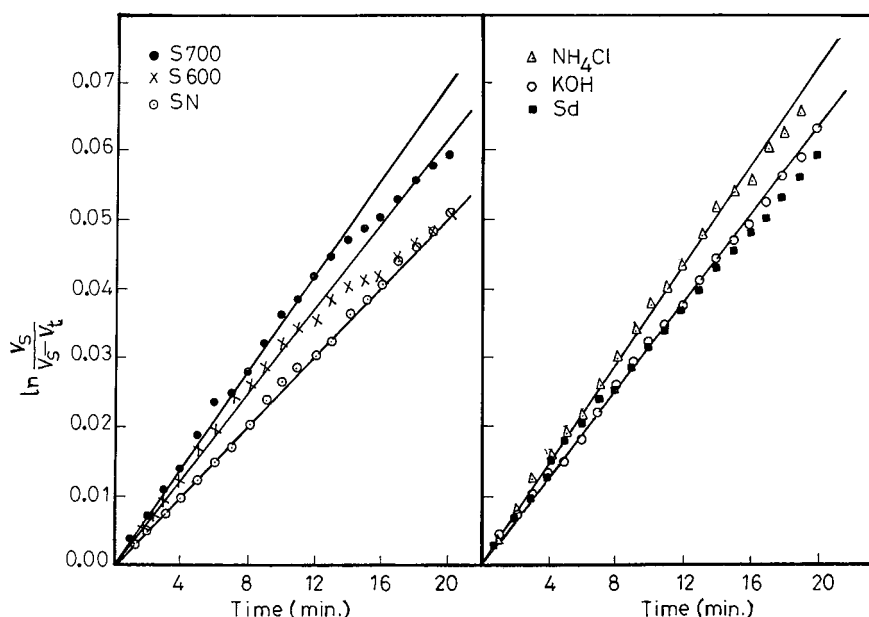


Figure 4. First order plots for decomposition of H<sub>2</sub>O<sub>2</sub> on activated carbon.

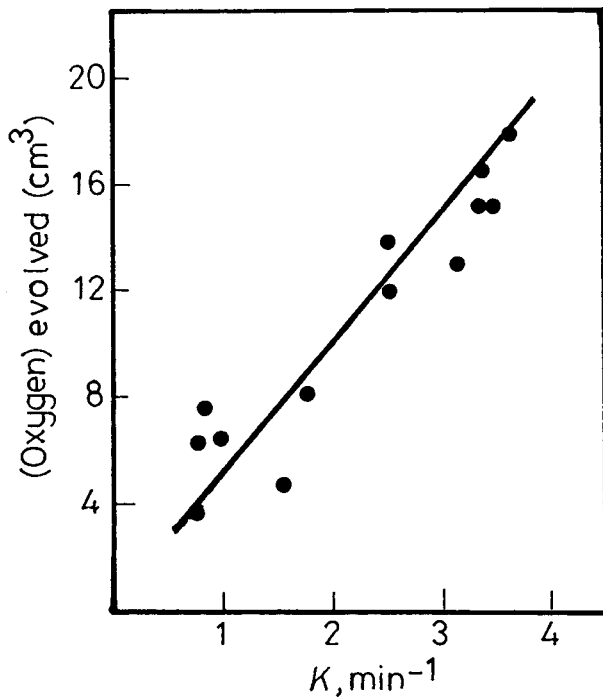


Figure 5. Correlation between volume of oxygen evolved at 1 h and initial rate constant ( $k$ ).

the first group which have greater porosity; the two groups are: acid-activated carbons (group I) and steam- (or  $NH_4Cl$ )-activated carbons (group II). Further confirmation of these two groups is evident when the volumes of oxygen evolved are normalized to unit surface area, as shown in the last column of Table 2. A more intensified disparity appears between the acidic and the basic carbons. The first group exhibited activity as low as  $0.55$  to  $2.95 \times 10^{-2} \text{ cm}^3 \text{ m}^{-2}$ , whereas the second category showed distinctively higher activities of  $5.63$  up to  $15.4 \times 10^{-2} \text{ cm}^3 \text{ m}^{-2}$ . This further confirms the role of the chemical nature of the surface of the carbon in catalysing the disproportiona-

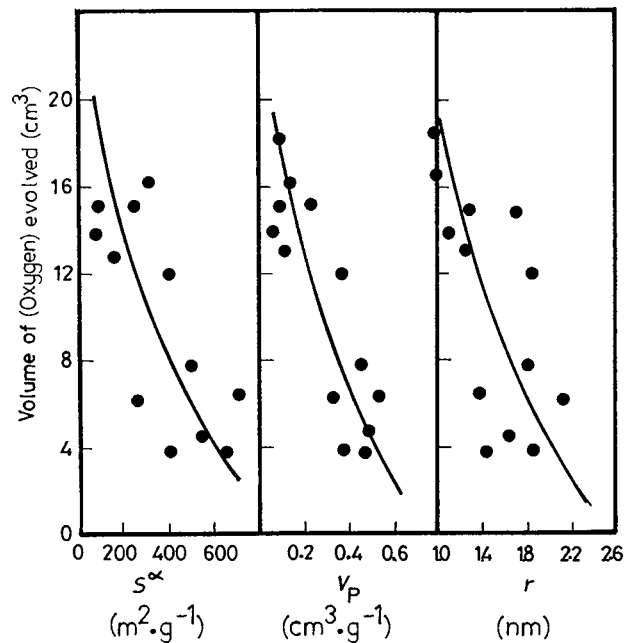


Figure 6. Relationship between  $V(O)$  at 1 h and carbon porosity characteristics.

tion of  $H_2O_2$ . We may recall, in this respect, the early investigation of Vasilenko,<sup>5</sup> who reported that upon acidification of the  $H_2O_2$  medium with  $HCl$ ,  $H_2SO_4$  or  $H_3PO_4$  at low pH, the former acids showed no effect whereas  $H_3PO_4$  reduced the rate of decomposition which was attributed to the formation of peracid. Thus, the presence of some contaminating residual activant ( $H_3PO_4$ ) inflicts an additional adverse effect on the decomposition of  $H_2O_2$  at the carbon surface. Here both surface functionalities ( $-COOH$  and  $PO_4^{3-}$ ) will play the main role in reducing the catalytic action.

Raising the heat treatment temperature, for the  $H_3PO_4$ -activated carbons, generally increases the decomposition in the initial and decay stages, but to

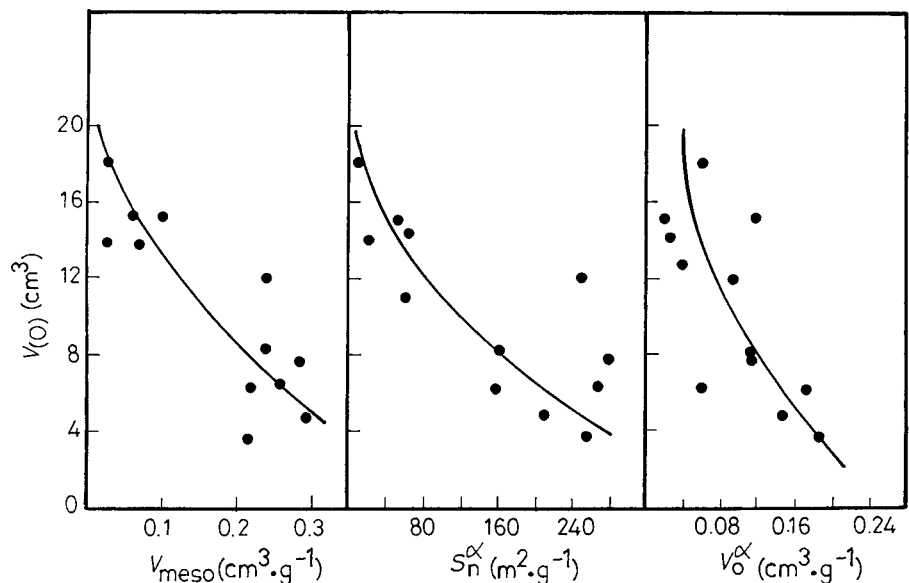


Figure 7. Correlation between  $V(O)$  and volume ( $V_{\text{meso}}$ ) or area of mesopores ( $S_n^x$ ), and volume of micropores ( $V_o^x$ ).

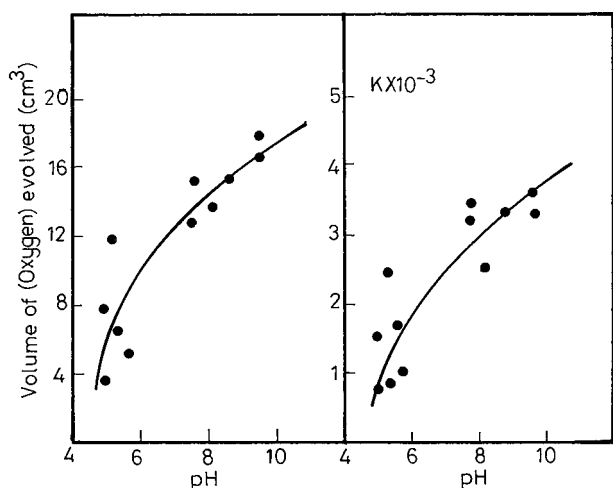


Figure 8. Correlation of *k* and *V*(O) on surface pH of the carbon.

no regular pattern (Figs 9 and 10). Also, increased impregnant concentration results in the reduction of activity, especially in the initial stage. It seems that low activant concentration, or higher temperature, produces carbons with higher catalytic activity towards H<sub>2</sub>O<sub>2</sub> decomposition. High activity at high heat-treatment temperatures could be due to the development of pores, making the diffusion of H<sub>2</sub>O<sub>2</sub> molecules, easier.

**DISCUSSION**

Heterogeneous decomposition of H<sub>2</sub>O<sub>2</sub> on activated carbon may be considered to depend on both carbon porosity and the chemical properties of the surface. The first would be associated with surface and bulk diffusion of the H<sub>2</sub>O<sub>2</sub> molecules. An extended surface and the development of porosity is thought to enhance the heterogeneous surface-catalysed reaction. On the other hand, the presence of surface functional groups, acquired during the preparation of the carbon or after treatment, would affect the disproportionation process. This reaction has been postulated to involve electron donation or acceptance mechanisms as well as

the free radical intermediates (hydroxyl OH<sup>-</sup> and peroxide OOH<sup>-</sup>).<sup>22,28-31</sup> This stresses the importance of the chemical structure of the surface of the activated carbon.

Regarding the effect of porosity on the extent of H<sub>2</sub>O<sub>2</sub> decomposition, it has been reported by some authors that catalytic dissociation carried out on buffered solutions showed a direct relationship between activity and surface area.<sup>1</sup> However, in other cases the lower-surface-area carbons produced higher decomposition rates for H<sub>2</sub>O<sub>2</sub> and catalytic activity was considerably increased when the carbon was degassed at gradually increasing temperatures.<sup>32,33</sup> This trend is strongly evident in the present study (Tables 1 and 2, Figs 6 and 7), where the activity appears to be progressively reduced with development of porosity. An adverse effect seems to be associated with the main textural parameters (total and non-microporous surface areas, total, meso- and micropore volumes and pore dimensions).

In the majority of previous studies, H<sub>2</sub>O<sub>2</sub> decomposition in media at various pH values was adjusted by buffered solutions. In the solution currently being investigated, it depends on the pH of the carbon slurry. The chemical nature of the surface, represented by the acidic/basic character of the carbon, proved to be the prevailing factor in affecting the rate and extent of H<sub>2</sub>O<sub>2</sub> decomposition (Fig 8). In reports over many decades, the rate of decomposition has been noticed to increase appreciably in certain pH ranges, and especially at and above pH 8. It was proposed that basic sites, composed of chromene groups, on the carbon surface initiated the chain reaction. At low pH these groups are oxidized to carbonium ions and the active carbon loses its catalytic activity. This was also confirmed upon subjecting the carbon to surface oxidation with either H<sub>2</sub>O<sub>2</sub> or HNO<sub>3</sub> which reduced the decomposition of H<sub>2</sub>O<sub>2</sub> considerably. The formation of surface carboxylic groups (—COOH) will accordingly retard the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> as it suppresses dissociation under these conditions.<sup>4-14</sup> Degassing at elevated temperatures resulted in decomposition of the acidic groups with an

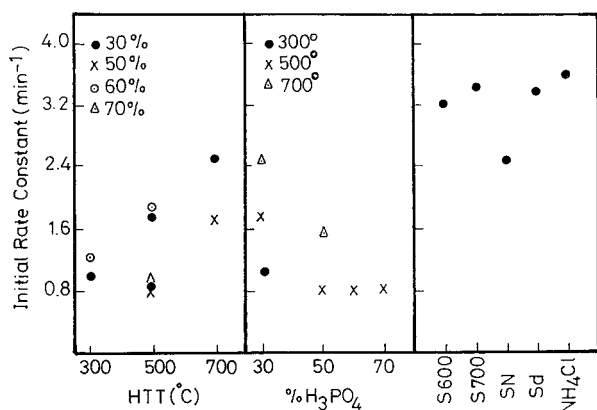


Figure 9. Dependence of initial rate constant (*k*) on conditions of active carbon preparation.

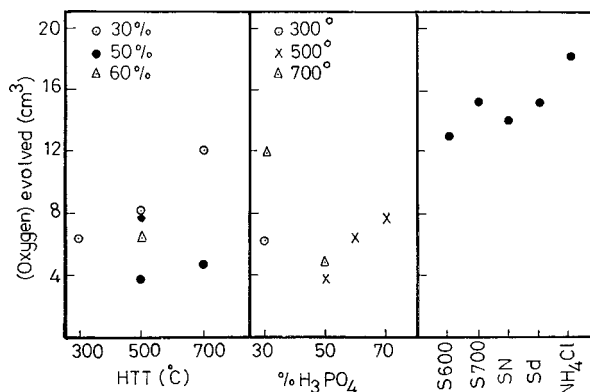
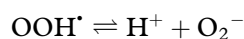
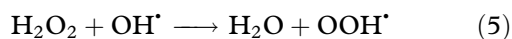


Figure 10. Dependence of volume of oxygen evolved at 1 h on conditions of active carbon preparation.

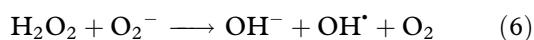
increased number of basic sites which consequently promotes catalytic activity.

Accordingly, H-type carbons, surface basicity, and high-pH media were found to be the most favourable in performing H<sub>2</sub>O<sub>2</sub> decomposition. Such behaviour may be attributed to many factors: (1) on H-type carbons (with basic nature) the available chromene groups initiate a chain mechanism of H<sub>2</sub>O<sub>2</sub> decomposition, (2) according to eqns (3) and (4), it is predicted that the dissociation of H<sub>2</sub>O<sub>2</sub> as a weak acid will be enhanced in alkaline media, whereas it will be suppressed in the acidic medium, (3) it was suggested that an acidic medium stabilized H<sub>2</sub>O<sub>2</sub> and an alkaline medium was conducive to its decomposition, (4) the OOH<sup>•</sup> radical, formed at low pH values, was postulated to be stabilized in the adsorbed state over the heterogeneous catalyst, and thus suppress the chain reaction.

At pH values higher than 8, H<sub>2</sub>O<sub>2</sub> tends to dissociate preferably into OH<sup>•</sup> and OH<sup>-</sup>, upon accepting an electron from the catalyst, and the OH<sup>•</sup> radical will dissociate more H<sub>2</sub>O<sub>2</sub> to give



The superoxide ion O<sub>2</sub><sup>-</sup> will decompose more H<sub>2</sub>O<sub>2</sub> in a chain reaction (known to be quite stable in aqueous solutions at high pH):<sup>28,29</sup>



Such a mechanism, involving free radicals (peroxide OOH<sup>•</sup> or hydroxyl OH<sup>•</sup>), thus describes how the heterogeneous decomposition of H<sub>2</sub>O<sub>2</sub> might be initiated and sustained. The ease of formation and stability of these free radicals becomes determined by the substrate medium. In the absence of a buffering solution, the nature of the surface of the tested active carbon will be the driving factor. Also, in absence of iron or manganese ions, as in the case of the Fenton reaction, the electron transfer process will originate from the carbon surface (electron donor or acceptor). The heterogeneous catalyst, activated carbon, will furnish the aqueous solution with H<sup>+</sup> ions or otherwise, such that the substrate medium acquires an acidic or basic character.

The displayed data thus appear to confirm the above postulates, where the catalytic dissociation of H<sub>2</sub>O<sub>2</sub> in the presence of activated carbon is essentially a function of slurry pH. High temperature carbons (steam-, CO<sub>2</sub>-, or NH<sub>4</sub>Cl-activated) are more favourable H<sub>2</sub>O<sub>2</sub>-decomposers, although they have a much lower surface area. The porosity developed does not seem to enhance the catalytic process. Traces of residual phosphates apparently adds to the inhibiting action of the acidic carbons obtained at lower temperatures, by chemical activation. It is noteworthy to mention that the maximum attained activity (~10% decomposition) is much higher than that reported for

the commercial carbon F-300, although it is less than 50% in comparison to two other carbons (ROW, GCW) produced by Norit.<sup>22</sup>

## CONCLUSION

Catalytic decomposition of H<sub>2</sub>O<sub>2</sub>, associated with release of oxygen gas, seems to be effectively catalysed by activated carbons derived from olive oil mill wastes. Highly-developed activated carbons obtained by impregnation with H<sub>3</sub>PO<sub>4</sub>, and heat-treated at 300–700 °C, showed low to moderate catalytic action. Carbons activated with steam as well as NH<sub>4</sub>Cl exhibited higher catalytic action as demonstrated by the initial rate constant, volume of evolved oxygen, percent decomposition, and the carbon dose required for complete decomposition of H<sub>2</sub>O<sub>2</sub>. Hydrogen peroxide decomposed to an extent independent of the porosity characteristics of the carbon, but seems related to the surface acidity/basicity, as well as conditions of preparation. Due to the intermediate formation of hydroxyl radicals, superoxide ions, and/or peroxide anions, the reaction is a function of the pH of the carbon surface rather than the porosity developed. The results confirm the driving role of the chemical nature of the surface in governing the catalytic action of activated carbon on H<sub>2</sub>O<sub>2</sub> decomposition.

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