

EFFECT OF H₂ TREATMENT ON THE ACTIVITY OF ACTIVATED CARBON FOR THE OXIDATION

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Abstract

In this work, hydrogen peroxide reactions, i.e. H₂O₂ decomposition and oxidation of organics in aqueous medium, were studied in the presence of activated carbon. It was observed that the carbon pre-treatment with H₂ at 300, 500, 700 and 800 °C resulted in an increase in activity for both reactions. The carbons were characterized by BET nitrogen adsorption, thermogravimetric analyses (TG), temperature programmed reduction (TPR), electron paramagnetic resonance (EPR), iodometric titration and determination of the acid/basic sites. TPR experiments showed that activated carbon reacts with H₂ at temperatures higher than 400 °C. The treatment produces a slight increase in the surface area. EPR analyses indicate the absence of unpaired electrons in the carbon. Iodometric titrations and TG analyses suggested that the treatment with H₂ generates reduction sites in the carbon structure, with concentration of approximately 0.33, 0.53, 0.59, 0.65 and 0.60 mmol/g for carbons treated at 25, 300, 500, 700 and 800°C, respectively. It was also observed the appearance of basic sites, which might be related to the reduction sites. It is proposed that these reducing sites in the carbon can activate H₂O₂ to generate HO radicals, which can lead to two competitive reactions, i.e. the hydrogen peroxide decomposition or the oxidation of organics in water.

Introduction

The surface chemistry of activated carbons has been extensively studied due to its importance for any applications (Boehm, 1966; Bansal et al., 1998; Radovic and Reinoso, 1997; Figueiredo et al., 1999; Lopez-Ramon et al., 1999; Chen and Zeng, 2003). Carbon functionalization with oxygen, nitrogen and sulfur groups has been widely investigated (Rios et al., 2003; Leon y Leon and Radovic, 1994; Reinoso and Sabio, 1998; Bohem, 2002). Oxygen surface groups are by far the most important influencing the properties of carbons. These oxygen surface groups can be formed during the activation or can be introduced on the carbon surface by different oxidizing treatments. Several properties of carbons such as hydrophilicity, acidic, redox and catalytic are directly correlated to surface oxygen containing groups such as carboxylic, phenolic, lactone, ether, pyrone, chromene, etc. Some examples of catalytic properties of carbons assigned to oxygen containing groups are: dehydration and dehydrogenation of alcohols (Szymanski and Rychlicki, 1991), oxidative dehydrogenation of ethylbenzene to styrene (Lisovskii and Aharoni, 1994), oxidation of Fe(II) by oxygen (Ahumada et al., 2002; Likholobov et al., 1995), oxidation of cobalt complexes by H₂O₂ (Kimura and Miyamoto, 1994), O₂ reduction to peroxide (Biniak et al., 2002; Yang and McCreery, 2000), activation of O₃ (Jans and Hoigne, 1998) and the decomposition of H₂O₂ to O₂ (Falcon and Carbonio, 1992; Grajek et al., 2001; Khalil et al., 2001; Radeke et al., 1989; Heil et al., 1972). These catalytic active carbons have been produced by oxidation reactions which, depending on the oxidizing agent and the conditions employed, might lead to different surface oxygenated groups (Figueiredo et al., 1999; Lopez-Ramon et al., 1999; Chen and Zeng, 2003). In this work it is reported that a reducing treatment with H₂ can also strongly modify the redox properties of an activated carbon, resulting in a remarkable effect on the catalytic properties towards the decomposition of H₂O₂ and the oxidation of organics in water. The oxidation of organic contaminants in aqueous medium using H₂O₂ promoted by activated carbons has been studied recently (Ince and Apikyan, 2000; Ince et al., 2002; Lucking et al., 1998). An interesting feature of activated carbons is that they can act as an adsorbent for the organic compound and also as catalyst/promoter for its oxidation. The generation of the active oxidizing species on the carbon surface near to the pre-concentrated contaminant can potentially

increase the process efficiency. The understanding of the reaction mechanism, the nature of the active site and the improvement of the carbon activity for this type of reaction are of considerable interest.

Methods

Activated carbon (Aldrich Darco G60, 100 mesh, American Norit), extensively washed with concentrated HCl and HF (ash content ca. 0.2%), was placed in a quartz tube under H_2 flow (100 ml min^{-1}) and treated in an oven at 300, 500, 700 and 800°C during 1 h. The carbons were characterized by N_2 adsorption/desorption (Autosorb 1 Quantachrome), thermal analysis (TG, Shimadzu TGA 50H) in airflow 10°Cmin^{-1} , temperature programmed reduction (TPR) ChemBet 3000 Quantachrome. Peroxide H_2O_2 decomposition tests were carried out in a volumetric glass system with 30 mg of the activated carbon in 7 ml solution of hydrogen peroxide 3 mol l^{-1} . The hydrogen peroxide decompositions were also carried out in the presence of organic compounds utilizing 7 ml solutions 0.05 g l^{-1} of textile dye Drimarem Red, methylene blue, hydroquinone and phenol. The oxidation of the textile dye Drimarem Red (CI 18286) (10 ml of a 0.05 g l^{-1} solution) and H_2O_2 with 60 mg of activated carbon was monitored by UV/Vis spectrophotometer Beckman DU 640 measurements. All these oxidation experiments were carried out at pH 6, adjusted with diluted HCl solution. For the iodometric titrations 20 mg of activated carbon was mixed with 10 ml of I_2 and backtitrated with $Na_2S_2O_3$ ($0.0013 \text{ mol l}^{-1}$). The number of acid sites was determined by the reaction of 30 mg of carbon with 25 ml of NaOH solution (0.02 mol l^{-1}) and titration of base excess with a HCl solution. The basic sites were determined by reaction of 30 mg of carbon with HCl (0.02 mol l^{-1}) and titration of the excess acids with NaOH.

Results and discussion

Hydrogen peroxide decomposition

The hydrogen peroxide decomposition (Eq. (1)) was studied in the presence of the activated carbons treated with H_2 at different temperatures and the results are displayed in Fig. 1.

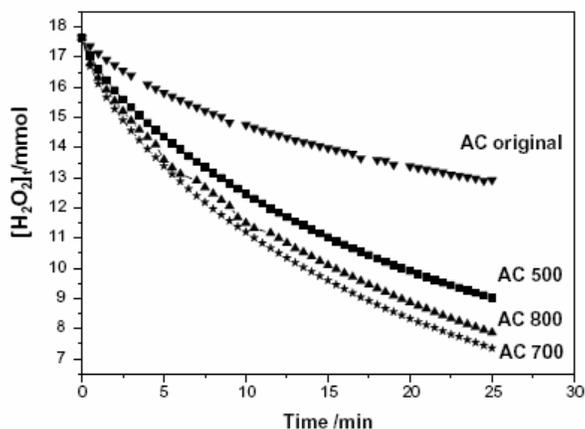


Figure 1. Hydrogen peroxide decomposition in the presence of the activated carbon treated with H_2 at different temperatures.

Kinetic analysis of the data shown in Fig. 1 suggests that the decomposition shows a first order dependence on the H_2O_2 concentration with rate constant of 0.015, 0.029, 0.037 and 0.035 min^{-1} for the original activated carbon and after treatment at 500, 700 and 800°C . It can be observed that the decomposition rate constant increases almost linearly up to 700°C but decreases upon treatment at 800°C . The activated carbons treated under N_2 flow did not show any significant increase in activity. The decomposition was also studied in the presence of different organic compounds such as phenol, hydroquinone, and the textile dye Drimarem Red dissolved in the reaction medium (Fig. 2). It can be observed that the decomposition is strongly inhibited specially by phenol followed by hydroquinone and the Drimarem Red dye. These results suggest that the organic compounds are participating in competitive processes during the H_2O_2 decomposition. These competitive processes might be related to (i) the adsorption of the organics on the active sites of the carbon and/or (ii) the reaction of the organic compounds with intermediate species in the H_2O_2 decomposition reaction. For example, phenol and hydroquinone, which are radical scavengers, might be reacting with radical

intermediates such as HO^\bullet and HOO^\bullet , which have been proposed to be formed during the H_2O_2 decomposition cycle (Falcon and Carbonio, 1992; Grajek et al., 2001; Khalil et al., 2001; Radeke et al., 1989; Heil et al., 1972).

Oxidation of the textile dye Drimarem Red

It was also studied the oxidation of the textile dye Drimarem Red by H_2O_2 in the presence of the activated carbon treated with H_2 at different temperatures. The reaction was monitored spectrophotometrically by the discoloration of the solution (Fig. 3). Control experiments with the original carbon and the AC 700°C in the absence of H_2O_2 were carried out to investigate the contribution of adsorption in the discoloration process. It can be observed similar results for both carbons where the absorbance decreases slowly reaching 0.7 after 4 h adsorption. Similar adsorptions of the textile dye were observed onto the carbons treated with H_2 at different temperatures. Also no significant discoloration was observed after 4 h reaction in the presence of H_2O_2 in the absence of carbon. In the presence of H_2O_2 and the original AC a significant color removal takes place showing that the carbon is promoting the dye oxidation by the peroxide. On the other hand, for the carbons AC 700°C and AC 800°C the discoloration is greatly increased, especially in the first 30 min reaction. These results suggest that the treatment with H_2 at 700 and 800°C produces an increase on the activity for the oxidation of the textile dye with H_2O_2 .

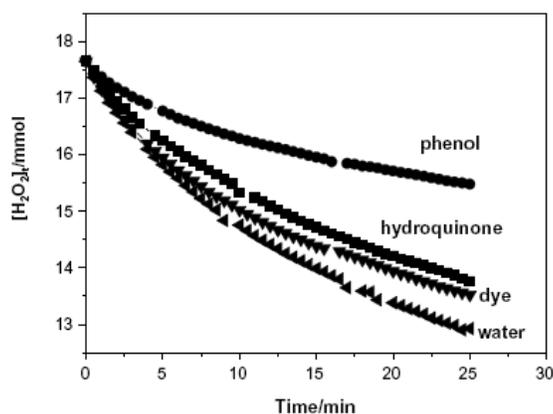


Figure 2. Hydrogen peroxide decomposition in the presence of phenol, hydroquinone, and the textile dye Drimarem Red using the original activated carbon.

Oxidation of the textile dye Drimarem Red

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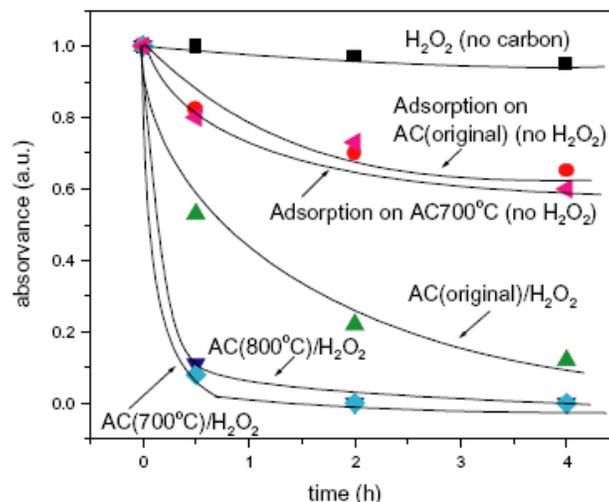


Figure 3. Oxidation of the textile dye Drimarem Red with (■) H_2O_2 solely, and H_2O_2 in the presence of the (▲) original activated carbon and the carbon treated with H_2 at (▼) 700 and (◆) 800°C. Adsorption on the (●) original activated carbon and on (◊) AC 700°C.

Table 1. Bet surface area, the microporous volume and area for the carbons treated with H_2 at 300 (AC 300), 700 (AC 700) and 800°C (AC 800).

| Samples | $S_{\text{BET}}/\text{m}^2\text{g}^{-1}$ | Microporous volume/ cm^3g^{-1} |
|-------------|--|--|
| Original AC | 783 | 0,20 |
| AC 300 | 820 | 0,21 |
| AC 500 | 821 | 0,21 |
| AC 700 | 828 | 0,22 |
| AC 800 | 811 | 0,21 |

BET surface area and porosity for the H_2 treated activated carbons

The BET surface area, the microporous volume and area for the carbons treated with H_2 at different temperatures are shown in Table 1. It can be observed that no significant modification on the surface area nor on the porosity occurred upon thermal treatment with H_2 even at 800°C.

Temperature programmed reduction (TPR) and electron paramagnetic resonance (EPR) studies

The temperature programmed reduction (TPR) experiments were carried out to investigate the reaction of the carbon with hydrogen during the thermal treatments. In the TPR experiments the carbon sample is heated at 10°Cmin^{-1} up to 900°C under hydrogen flow and the H_2 consumption monitored continuously. The obtained TPR profile is displayed in Fig. 4. The obtained TPR clearly shows that the activated carbon reacts with H_2 . It can be observed in the TPR for the original carbon that the hydrogen consumption starts at approximately 400°C and increases sharply with an intense peak between 600 and 800°C . It is interesting to observe that the TPR of the carbon pretreated at 700 and 800°C did not show any significant H_2 consumption. On the other hand, the carbon pretreated at 500°C with H_2 showed a small peak at temperatures higher than 500°C in the TPR experiment. These results suggest that the pre-treatment at 700 and 800°C leads to a complete reaction with H_2 whereas at 500°C only a partial reaction with H_2 had occurred. Although the nature of the H_2 reaction with carbon is not clear, a detailed TPR and TPD work carried out by Calo et al., 1997 and Roman-Martinez et al., 1993 showed that hydrogen can react with oxidized carbons during thermal desorption of oxygen surface complexes. The authors propose that hydrogen is consumed by chemisorbing on reactive nascent sites created by the decomposition of the oxygen containing groups. Although the carbon used in the present work is not oxidized and does not contain a high concentration of oxygen surface groups, these hydrogenation processes might be playing an important role during TPR experiments. EPR analyses of all the carbons studied in this work did not show any significant signal, suggesting the absence of unpaired electrons in the carbon structure.

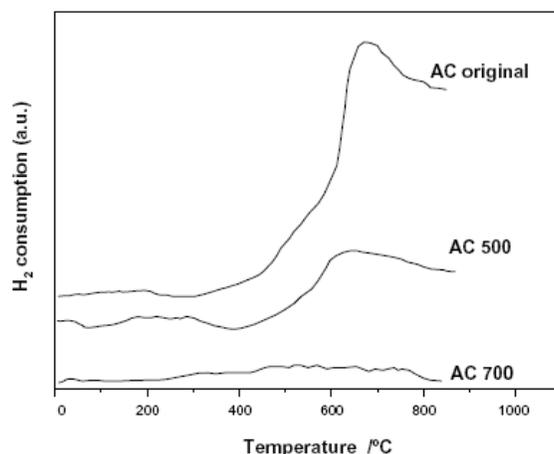
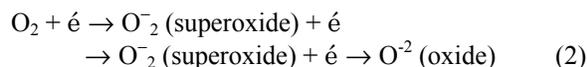


Figure 4. Temperature programmed reduction with H₂ of the original activated carbon and the carbon treated with H₂ at 500 and 700°C.

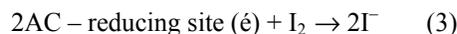
Thermogravimetric and iodometric analyses

The TG analyses in air of the AC treated with H₂ at different temperatures are shown in Fig. 5. It can be observed for the untreated carbon that no significant weight loss occurs up to 550°C. At 630°C a strong weight loss is observed related to the total oxidation of the carbon by oxygen in the air. Similar results were observed for the carbon treated at 300°C. On the other hand, an important feature is observed only for the carbons treated at 700 and 800°C, i.e. weight gains of 3.0% and 2.2%, respectively, in the temperature range 360–520°C. These weight gains are likely related to the incorporation of oxygen in the carbon structure. These results are in a good agreement with the work presented by Menéndez et al., 1996 that studied carbon treated with N₂ and H₂ up to 950°C and observed a strong oxygen adsorption on the obtained carbons even at room temperature. According to these authors, upon thermal treatment the carbon surface oxygen containing groups decompose leaving unsaturated carbon atoms at crystallite edges. Part of these unsaturated carbons reacts with H₂ producing stable basic sites, whereas other sites will be available for the reaction with O₂. These basic sites have also been observed in the present work and will be described below. The activation and incorporation of O₂ gaseous molecules has been suggested to take place via a stepwise reduction to form superoxide, peroxide and finally the oxide (Eq. 2).

One can envisage that the electrons used for the oxygen reduction were probably produced by the reaction with H₂ at high temperature. To quantify the reducing sites it was used iodometric titrations. The reducing sites reacted with iodine (I₂) according to the equation:



The effect of the H₂ treatment on the concentration of these reducing sites is shown in Fig. 6. It can be observed that the concentration of reducing sites increases as the carbons are treated with H₂ at 300, 500 and 700°C. On the other hand, at 800°C a slight decrease on the concentration of the reducing sites occurs.



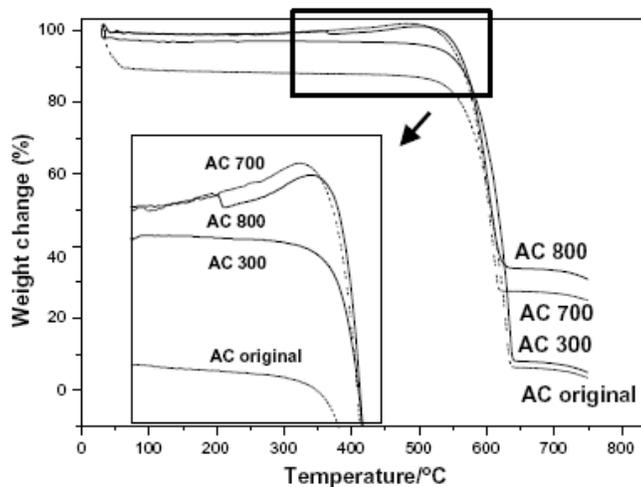


Figure 6. Concentration of reducing sites obtained by iodometric titrations for the AC treated with H₂ at 300, 500, 700 and 800°C.

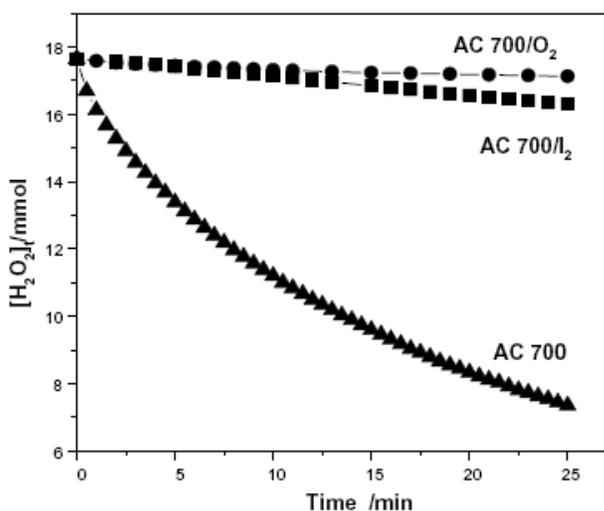


Figure 7. Hydrogen peroxide decomposition in the presence of the AC/H₂ (700°C) previously treated with O₂ and with I₂.

To investigate the participation of these reducing sites on the H₂O₂ decomposition, the carbon treated with H₂ at 700°C was submitted to two different treatments: (i) oxygenation at 360°C and (ii) reaction with I₂. These reactions should eliminate the reducing sites. The H₂O₂ decompositions in the presence of the carbons AC/H₂ (700°C) treated with O₂ and with I₂ are shown in Fig. 7. It can be observed that after reaction with O₂ or I₂ the peroxide decomposition is strongly reduced, suggesting that the reducing sites play an important role in the decomposition. Another important feature observed in the TG of the carbons treated at 700 and 800°C is that the weight loss due to the total oxidation, which is approximately 100% for the original AC, strongly decreases to 76% and 70%, respectively. These results suggest that the pre-treatment with H₂ produced a more thermally stable form of carbon, which cannot be oxidized even at temperatures as high as 750°C. This is probably related to the organization of the carbon structure producing a graphitic/ pyrolytic structure, which is highly stable upon oxidation at high temperatures.

Acid and basic sites in the activated carbons treated with H₂

The concentration of acid and basic sites was determined in the carbons by simple acid and base titration. The results are displayed in Fig. 8. The original activated carbon possesses approximately 0.48 mmol g⁻¹ of acid sites. It can be observed that the treatment at 300°C led to a strong decrease of the acid sites. These results suggest that these acid sites are likely related to surface carboxylic acid, which decomposes at temperatures relatively low (Figueiredo et al., 1999; Bohem, 2002). Upon treatment at 500°C the number of acid sites further decreases but no significant decrease is observed at higher temperatures. It can also be observed that the original activated carbon shows basic sites at approximately 0.29 mmol g⁻¹. It is interesting to observe that the concentration of basic sites increases almost linearly up to 0.48 mmol g⁻¹ upon treatment with H₂ at 300 and 500°C. On the other hand, treatment at 700 and 800°C does not lead to an increase on the basic site concentration. Basic sites present in the carbon structure have been related to oxygen functionalities such as pyrones, chromenes, ethers and carbonyls. However, as the H₂ treatment should produce a decrease on the oxygen content of the carbons due to thermal decomposition and hydrogenation, the increase in the basic site concentration is likely not related to oxygen surface groups but probably to Lewis basic sites. These Lewis sites have been assigned to *p* electron rich regions within the basal planes of the graphitic microcrystals (Menéndez et al., 1996). It is interesting to observe a good correlation of basic sites and the reduction sites, which suggests that the Lewis basic sites might have an important role during the reduction process. This modification of the acid/basic character of the carbon upon H₂ treatment should produce an important modification of the surface charge balance. As observed by Menéndez et al., 1996 the increase in the basic sites concentration should lead to an increase of the pH point of zero charge. However, it is interesting to observe in Fig. 3 that the adsorption of the anionic Drimarem Red dye was not significantly affected by the modification of the surface acid/basic character.

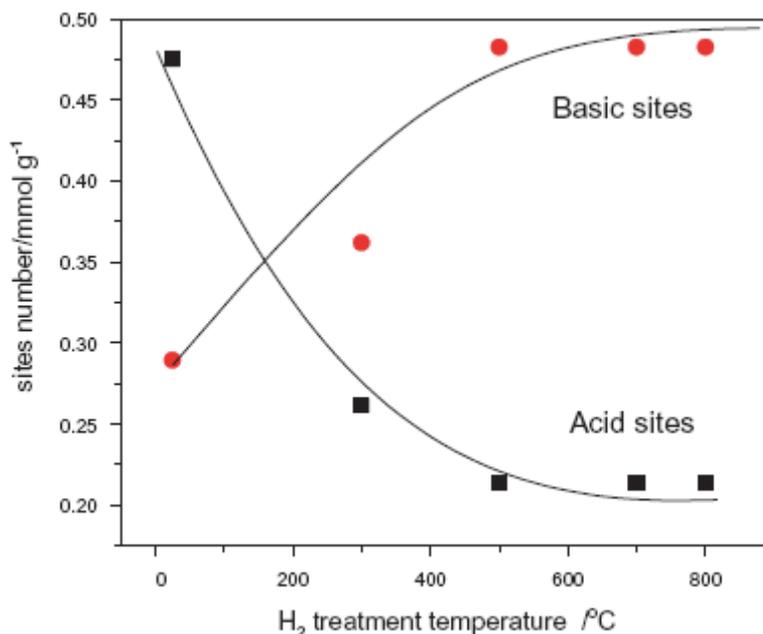


Figure 8. Acid and basic sites in the activated carbons treated with H₂ at different temperatures.

Reaction mechanism

Although the H₂O₂ decomposition mechanism is not completely understood, several electron transfer processes have been suggested to take place during the reaction. According to these mechanisms, the reaction might be initiated by a reducing site transferring an electron to H₂O₂ to produce a HO• radical or by the reaction of peroxide transferring an electron to an oxidizing site yielding a HOO• species (Biniak et al., 2002; Yang and McCreery, 2000; Jans and Hoigne, 1998; Falcon and Carbonio, 1992; Grajek et al., 2001; Khalil et al., 2001; Radeke et al., 1989; Heil et al., 1972). In this work, both reactions, i.e. H₂O₂ decomposition and oxidation of organics by H₂O₂, are likely taking place via radicals as suggested by the inhibition effect observed during the H₂O₂ decomposition by the presence of organics such as phenol, hydroquinone and the Drimarem Red textile dye. A simple competitive mechanism can be proposed for the H₂O₂ reactions in the presence of the activated carbon (Fig. 9). The reactions initiate by the activation of H₂O₂ by a reducing site in a Fenton like reaction (Ince and Apikyan, 2000; Ince et al., 2002; Lucking et al., 1998) to produce a HO•

radical intermediate. This hydroxyl radical can then react according to two competitive pathways: (i) pathway 1, reacting with another H_2O_2 molecule leading to the decomposition to O_2 , and (ii) pathway 2, oxidation of organic molecules present in the aqueous medium.

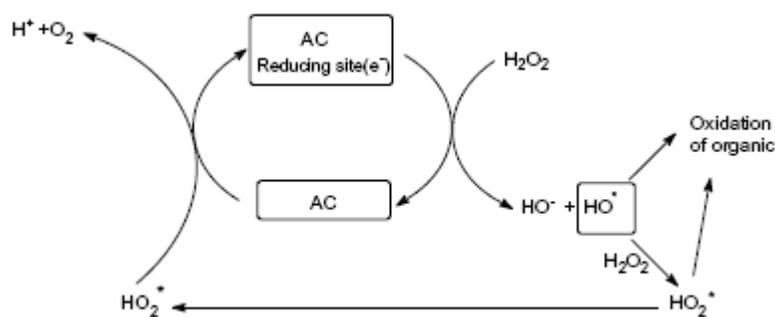


Figure 9. Proposed competitive mechanism for the H_2O_2 reactions in the presence of the activated carbon.

Conclusion

The results obtained in this work show that the chemical properties of activated carbon can be strongly modified by a treatment with H_2 . The reduction with H_2 in the temperature range $450\text{--}800^\circ\text{C}$ creates relatively high concentration of reducing sites, which can reduce O_2 and I_2 . These reducing sites can also promote the decomposition of H_2O_2 and the oxidation of organic compounds in aqueous medium by H_2O_2 . These reactions seem to take place via a radicalar mechanism probably initiated by an electron transfer from the reducing site to H_2O_2 to produce species such as HO^\bullet and HOO^\bullet .

Acknowledgements

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