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## Exploring the activity of chemical-activated carbons synthesized from peach stones as metal-free catalysts for wet peroxide oxidation

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### ABSTRACT

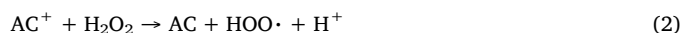
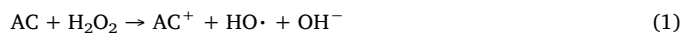
Peach stones were used as raw material for the synthesis of activated carbons with different properties. Firstly, peach stones were chemically activated using a 12 M H<sub>3</sub>PO<sub>4</sub> solution and carbonized under flowing air (400 °C). The obtained activated carbon, named as PS, is characterized by a high surface development (S<sub>BET</sub> = 1262 m<sup>2</sup> g<sup>-1</sup>) and acidic character (pH<sub>PZC</sub> = 4.2). A fraction of PS was further carbonized under N<sub>2</sub> atmosphere at 800 °C to remove surface functionalities and to increase its basicity (PS-800). In addition, a Pt catalyst supported on PS (3% w/w Pt/PS) was synthesized by incipient wetness impregnation, resulting in a considerable hydrophilicity increasing. The synthesized materials were tested in the catalytic wet peroxide oxidation (CWPO) of highly concentrated solutions of 4-nitrophenol (4-NP, 5 g L<sup>-1</sup>) during 24 h experiments, conducted at relatively mild operating conditions (T = 50–110 °C, pH = 3, catalyst load = 2.5 g L<sup>-1</sup> and [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 17.8 g L<sup>-1</sup>, corresponding to the stoichiometric amount of H<sub>2</sub>O<sub>2</sub> needed for the complete mineralization of 4-NP). It was observed that the increase of electron-donating functionalities in PS-800 promotes the generation of reactive HO· radicals, being the activity towards CWPO twice higher than that obtained with the pristine PS. Besides, increasing operating temperature substantially enhances CWPO, finding a 80% of 4-NP removal at 110 °C. On the other hand, despite the sharp increment in H<sub>2</sub>O<sub>2</sub> decomposition due to the presence of Pt particles in Pt/PS catalyst, this decomposition is inefficient in all cases, with a consequent poor pollutant removal. This can be attributed to the recombination of HO· radicals into non-reactive species –scavenging effects, promoted by the hydrophilicity of the catalyst.

### 1. Introduction

Catalytic wet peroxide oxidation (CWPO) relies on the oxidation of organic species using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and a suitable catalyst to promote the formation of HO· radicals, under relatively mild operation conditions (0.1–0.2 MPa, 20–130 °C) [1,2].

The classical heterogeneous catalysts employed in CWPO process consist on an active phase, mainly a transition metal like Fe, supported on a porous material, like activated carbon. However, metal leaching of the metallic phase to the reaction medium is usual with these catalysts, leading to a severe deactivation [3–6]. This has led to the exploration of metal-free materials capable to catalyze the decomposition of H<sub>2</sub>O<sub>2</sub> [7–10]. In this context, due to their electron donor-acceptor surface

properties, activated carbons have been used as catalysts in CWPO [10–15] since they allow H<sub>2</sub>O<sub>2</sub> decomposition into HO· radicals in a similar mechanism than the Fenton process, according to the following scheme, where AC and AC<sup>+</sup> represents, respectively, reduced and oxidized active sites existing at the surface of activated carbons:



The use of metal-free carbonaceous materials as catalysts has become important in recent years, constituting ca. 30% of the publications regarding the CWPO process (*Web of Science*). Nevertheless, among these studies, the pollutant oxidation is, in general, moderate, low

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activities being obtained for the removal of phenolic compounds [13–17], even when using doses of  $\text{H}_2\text{O}_2$  higher than the stoichiometric. Besides, the removal of organic pollutants using these catalytic proceeds mostly through pollutant adsorption [1,12,15,17–22]. On the other hand, radical recombination is common in these studies, affecting the efficient consumption of  $\text{H}_2\text{O}_2$  into  $\text{HO}\cdot$  radicals, since non-reactive species like  $\text{H}_2\text{O}$  and  $\text{O}_2$  are formed [23].

Different authors have tried to improve the properties of activated carbons for CWPO through chemical modification of their surface [11–14,16,24], since basic groups enhance  $\text{H}_2\text{O}_2$  decomposition and acid groups withdraw electrons from the carbon surface, hindering their use in  $\text{H}_2\text{O}_2$  attack, which may result in the restriction of secondary reactions like radicals recombination [8,12–15,24–28].

The analysis of the scientific literature reveals that activated carbons have been synthesized through both, physical and chemical activation methods, from different lignocellulosic residues, like wood, bamboo, sawdust, nuts, cherry stones, peach stones, rice husk, almond shells, peanut shells, potato peels or coffee wastes, among others, with good mechanical and porous properties [29–31]. In this study, peach stones are used as raw material for the synthesis of activated carbons with different surface properties, evaluating their performance as catalysts in the CWPO of wastewaters with high pollutant concentration. A 4-nitrophenol (4-NP,  $5\text{ g L}^{-1}$ ) model solution was used to mimic highly polluted wastewaters.

## 2. Materials and methods

### 2.1. Chemicals

Peach stones were collected from a local agricultural company (Madrid, Spain) producing peach syrup. 4-NP (98 wt.%) was purchased from Acros Organics.  $\text{H}_2\text{O}_2$  (30%, w/v) was obtained from Fluka. Sodium hydroxide (NaOH, 98 wt.%) was acquired from Panreac. Acetic acid (glacial acetic acid), acetonitrile and methanol (all HPLC grade, 99.99 wt.%) were purchased from Fisher Chemical. Hydrochloric acid (HCl, 37 wt.%), titanium (IV) oxysulphate (15 wt.% in dilute sulphuric acid, 99.99%), sodium sulphite ( $\text{Na}_2\text{SO}_3$ , 98 wt.%), phosphoric acid (85 wt.%) and  $\text{H}_2\text{PtCl}_6$  were obtained from Sigma-Aldrich. All chemicals were used as received without further purification. Ultrapure water was used throughout the work.

### 2.2. Synthesis of carbon materials

An activated carbon was prepared by chemical activation of peach stones (previously crushed and sieved to a particle size between 0.5 and 1.0 mm), in a round-bottom flask reactor, using a  $\text{H}_3\text{PO}_4$  solution ( $12\text{ mol L}^{-1}$ ) as activating agent, at  $85\text{ }^\circ\text{C}$  for 6 h, in a mixture of  $200\text{ g L}^{-1}$ . After impregnation, the solid was filtered and calcined during 4 h in a vertical quartz reactor under air flow ( $50\text{ cm}^3\text{ min}^{-1}$ ) at  $400\text{ }^\circ\text{C}$ , defining a heating ramp of  $5\text{ }^\circ\text{C min}^{-1}$ . The resulting carbon was thoroughly washed with ultrapure water to remove the remaining phosphoric acid, until a pH close to neutrality was reached. Finally, the solid was dried in an oven at  $110\text{ }^\circ\text{C}$  for 24 h. The resulting carbon, ground to particle sizes in the range 100–250  $\mu\text{m}$ , was named as PS. As it will be shown in the Results and Discussion Section, this material presents acid character. In order to improve its catalytic properties for wet peroxide oxidation process, two strategies have been followed. On the one hand, a fraction of PS was further calcined under  $\text{N}_2$  atmosphere ( $100\text{ cm}^3\text{ min}^{-1}$ ) for 4 h at  $800\text{ }^\circ\text{C}$ , to remove surface functionalities, increasing the basicity of the carbon. This material was named as PS-800. On the other hand, a metallic Pt catalyst supported on PS was synthesized by incipient wetness impregnation method, using a  $\text{H}_2\text{PtCl}_6$  aqueous solution of the required concentration to obtain 3% w/w active phase nominal loading in the catalyst. After drying at  $110\text{ }^\circ\text{C}$  overnight, the activation of the catalyst was carried out by reduction under  $\text{N}_2/\text{H}_2$  ( $150:50\text{ cm}^3\text{ min}^{-1}$ ) continuous flow at  $350\text{ }^\circ\text{C}$  for 3 h. This catalyst was named as Pt/PS.

### 2.3. Characterization

Elemental analyses were performed on a LECO CHNS-932 analyzer. Bulk Pt content was determined using X-ray fluorescence (XRF, S4 Explorer, Bruker).

Pt dispersion on the catalyst surface was determined by CO chemisorption at room temperature (PulseChemiSorb 2705, Micromeritics). The stoichiometry of the CO adsorption on the metallic atoms was assumed to be 1.

X-ray diffraction (XRD) patterns were obtained in a X'Pert-MPD diffractometer (PANalytical), using Cu K $\alpha$  monochromatic radiation (0.154056 nm), a scanning range of  $5\text{--}100^\circ$  and a scan step size of  $0.1^\circ$  with 1 s collection time.

The porous structure of the catalysts was characterized by  $\text{N}_2$  adsorption-desorption isotherms at  $-196\text{ }^\circ\text{C}$  and  $\text{CO}_2$  adsorption-desorption isotherms at  $0\text{ }^\circ\text{C}$  (Tristar II 3020, Micromeritics). The samples were previously outgassed for 12 h at  $150\text{ }^\circ\text{C}$  at a residual pressure of  $10^{-3}$  Torr (VacPrep 061, Micromeritics). The specific surface area ( $S_{\text{BET}}$ ) was calculated by BET equation. The micropore surface area ( $S_{\text{micro}}$ ), mesopore surface area ( $S_{\text{meso}}$ ) and micropore volume ( $V_{\text{micro}}$ ) were estimated by the *t*-plot method and the mesopore volume ( $V_{\text{meso}}$ ) was determined by subtracting  $V_{\text{micro}}$  value from the total  $\text{N}_2$  amount adsorbed at  $P/P_0 = 0.95$  [32–34]. The pore size distribution of the materials was obtained by using the Non-Local Density Functional Theory [35].

The pH of point of zero charge ( $\text{pH}_{\text{PZC}}$ ) was determined by pH drift tests adapting the procedure described elsewhere [36]. Five NaCl (0.01 M) solutions were prepared as electrolyte with varying initial pH, in the range 2–11 (using HCl and NaOH 0.1 M solutions). 0.05 g of carbon sample was contacted with 20 mL of each NaCl solution. The equilibrium pH of each suspension was measured after 48 h under stirring (200 rpm) in an orbital shaker at room temperature. The  $\text{pH}_{\text{PZC}}$  value was determined by intercepting the curve ‘final pH vs initial pH’ with the main diagonal of the plot (final pH = initial pH) [37].

Temperature programmed desorption (TPD) analyses were performed by heating 0.1 g of the carbon sample from  $25\text{ }^\circ\text{C}$  up to  $1100\text{ }^\circ\text{C}$  ( $5\text{ }^\circ\text{C min}^{-1}$ ), in a quartz tube reactor, under constant  $\text{N}_2$  flow ( $1000\text{ cm}^3\text{ min}^{-1}$ ). The evolving concentrations of CO and  $\text{CO}_2$  were monitored using a SIEMENS Ultramat 22 gas analyzer. The peaks deconvolution of the TPD profiles were adjusted to multiple Gaussian functions by Origin Pro 9.0 software, according to the literature [38].

Fourier Transform Infrared Spectroscopy (FT-IR) was performed in a Thermo Nicolet spectrophotometer, recording spectra in a wavelength range of  $400\text{--}4600\text{ cm}^{-1}$ .

### 2.4. 4-Nitrophenol removal experiments

The CWPO runs were carried out in a batch reaction system described elsewhere [23], consisting of a 250 mL glass reactor with a sample collection port, magnetically stirred (600 rpm), immersed in an oil bath with temperature control and equipped with a reflux condenser. In a typical experiment, the reactor was loaded with 50 mL of a highly concentrated 4-NP aqueous solution ( $5\text{ g L}^{-1}$ ) and heated up to the desired temperature ( $50\text{ }^\circ\text{C}$  or  $80\text{ }^\circ\text{C}$ ). Initial pH was adjusted to 3 using  $\text{H}_2\text{SO}_4$  and NaOH 0.1 M solutions, and the stoichiometric concentration of  $\text{H}_2\text{O}_2$  needed to mineralize completely 4-NP was added to the system ( $17.8\text{ g L}^{-1}$ ). The reaction started with the addition of  $2.5\text{ g L}^{-1}$  of catalyst. During the experiment, small aliquots were periodically withdrawn from the reactor, typically at 0, 5, 15, 30, 60, 120, 240, 480 and 1440 min, for analysis. A blank experiment, *i.e.* without catalyst, was carried out to assess possible non-catalytic oxidation reactions promoted by  $\text{H}_2\text{O}_2$ .

A set of experiments was carried out at higher temperature ( $110\text{ }^\circ\text{C}$ ), using a stoppered 500 mL glass batch reactor (Büchi), equipped with a backpressure controller. First, the reactor was loaded with 150 mL of  $5\text{ g L}^{-1}$  4-NP aqueous solution at pH 3 and  $2.5\text{ g L}^{-1}$  of catalyst. Once

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