



# 4-Hydroxyphenylacetic acid oxidation in sulfate and real olive oil mill wastewater by electrochemical advanced processes with a boron-doped diamond anode



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## HIGHLIGHTS

- Degradation of 4-hydroxyphenylacetic acid spiked in 0.050 M Na<sub>2</sub>SO<sub>4</sub> and in real OOMW.
- Quicker mineralization in the order AO-H<sub>2</sub>O<sub>2</sub> < EF < PEF in all media using a BDD anode.
- Pseudo-first-order decay of 4-hydroxyphenylacetic acid in all treatments.
- Almost total mineralization achieved by the powerful PEF process in 0.050 M Na<sub>2</sub>SO<sub>4</sub>.
- Up to 80% mineralization with strong biodegradability enhancement in the real OOMW matrix.

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## ABSTRACT

The degradation of 4-hydroxyphenylacetic acid, a ubiquitous component of olive oil mill wastewater (OOMW), has been studied by anodic oxidation with electrogenerated H<sub>2</sub>O<sub>2</sub> (AO-H<sub>2</sub>O<sub>2</sub>), electro-Fenton (EF) and photoelectro-Fenton (PEF). Experiments were performed in either a 0.050 M Na<sub>2</sub>SO<sub>4</sub> solution or a real OOMW at pH 3.0, using a cell with a boron-doped diamond (BDD) anode and an air-diffusion cathode for H<sub>2</sub>O<sub>2</sub> generation. Hydroxyl radicals formed at the BDD surface from water oxidation in all processes and/or in the bulk from Fenton's reaction between added Fe<sup>2+</sup> and generated H<sub>2</sub>O<sub>2</sub> in EF and PEF were the main oxidants. In both matrices, the oxidation ability of the processes increased in the order AO-H<sub>2</sub>O<sub>2</sub> < EF < PEF. The superiority of PEF was due to the photolytic action of UVA radiation on photosensitive by-products, as deduced from the quick removal of Fe(III)-oxalate complexes. The effect of current density and organic content on the performance of all treatments was examined. 4-Hydroxyphenylacetic acid decay obeyed a pseudo-first-order kinetics. The PEF treatment of 1.03 mM 4-hydroxyphenylacetic acid in 0.050 M Na<sub>2</sub>SO<sub>4</sub> allowed 98% mineralization at 360 min even at low current density, whereas 80% mineralization and a significant enhancement of biodegradability were achieved with the real OOMW.

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## 1. Introduction

The olive oil produced in Spain and other Mediterranean countries accounts for more than 75% of total world production. This, in turn, entails a huge annual release of industrial olive oil mill wastewater (OOMW). These effluents are usually acidic and extremely hazardous for the aquatic environment due to their very large organic matter contents and high turbidity levels, which cause

a poor oxygenation and light penetration [1,2]. OOMW mainly contains phenols, acids, lipids, sugars and tannins [3,4]. A limited number of works have described the treatment of these effluents by catalytic wet air oxidation [5] and electrolysis with a Pt anode [6,7], showing a significant destruction of phenolic components. More research efforts are then needed to degrade OOMW and its main single components to devise an optimum integral treatment for such industrial wastewater.

4-Hydroxyphenylacetic acid is a typical phenolic component routinely found in OOMW. It is a primary product formed upon oxidation of tyrosol (4-hydroxyphenylethanol), which is a well known phenolic compound in OOMW as well [8,9]. On the other hand,

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4-hydroxyphenylacetic acid is useful for the industrial synthesis of various end products like the  $\beta$ -blocker atenolol, among others. However, the information on its degradation routes and fate in the field of wastewater treatment is scarce. The removal of 4-hydroxyphenylacetic acid by advanced oxidation processes (AOPs) like zero-valent iron [10] and UV/H<sub>2</sub>O<sub>2</sub> and Fenton's reagent [11] has been reported. Conversely, as far as we know, its destruction by powerful electrochemical AOPs (EAOPs) has not been reported yet.

Over the last fifteen years, the EAOPs have received increasing attention to remove toxic and/or non-biodegradable organic pollutants from wastewater [12–15]. These methods are particularly viable owing to their environmental compatibility, high energy efficiency, versatility, amenability of automation, safe operation under mild conditions and easy scale-up. The great oxidation power of EAOPs is based on the continuous in situ generation of reactive oxygen species (ROS) like hydroxyl radical ( $\cdot\text{OH}$ ), the second strongest oxidant known after fluorine. A high standard reduction potential ( $E^\circ(\cdot\text{OH}/\text{H}_2\text{O})=2.80\text{ V}/\text{SHE}$ ) explains its ability to non-selectively react with most organics up to mineralization to CO<sub>2</sub>, water and inorganic ions [13,14].

The boron-doped diamond (BDD) thin-film anodes yield the quickest mineralization of organics in the EAOPs. This anode possesses larger oxidation ability than conventional Pt [16–18] and PbO<sub>2</sub> [19] ones as a result of the low adsorption of both,  $\cdot\text{OH}$  formed at its surface and organics, as well as its greater O<sub>2</sub>-evolution overvoltage. These properties allow the mineralization of aromatics [12,20–27] and by-products like short-chain linear carboxylic acids [28]. The oxidation ability of EAOPs may be upgraded when H<sub>2</sub>O<sub>2</sub> is continuously generated at the cathode from the two-electron reduction of O<sub>2</sub>, as follows [13,14]:



Anodic oxidation with electrogenerated H<sub>2</sub>O<sub>2</sub> (AO-H<sub>2</sub>O<sub>2</sub>), electro-Fenton (EF) and photoelectro-Fenton (PEF) are the most important EAOPs based on H<sub>2</sub>O<sub>2</sub> electrogeneration. They use effective carbonaceous cathodes for Reaction (1) like BDD [29], activated carbon fiber [30], carbon nanotubes [31], carbon sponge [32], carbon felt [9,24,33–35] and carbon-polytetrafluoroethylene (PTFE) gas-diffusion devices [27,36–39].

This paper presents a study on the oxidation of 4-hydroxyphenylacetic acid, spiked in either synthetic sulfate solutions with ultrapure water or real OOMW solutions, by AO-H<sub>2</sub>O<sub>2</sub>, EF and PEF using a BDD/air-diffusion tank reactor. Very worth mentioning, no previous studies have addressed the treatment of real OOMW by EAOPs with an air-diffusion cathode, which is mandatory aiming to scale-up these promising technologies. The effect of current density ( $j$ ) and substrate content on the degradation rate and mineralization current efficiency (MEC) was examined. The kinetics for the substrate decay and the evolution of generated carboxylic acids were monitored by high-performance liquid chromatography (HPLC). The change in biodegradability was determined during the treatment of OOMW. Gas chromatography-mass spectrometry (GC-MS) was used to identify the main organic components of the raw OOMW.

## 2. Experimental

### 2.1. Chemicals

4-Hydroxyphenylacetic acid (98% purity) was purchased from Sigma-Aldrich. Analytical grade oxalic acid was supplied by Merck. Iron(II) sulfate heptahydrate and anhydrous sodium sulfate were of analytical grade supplied by Fluka. Analytical grade sulfuric acid from Acros Organics was used to adjust the initial pH to 3.0.

Aqueous solutions were prepared with high purity water from a Millipore Milli-Q system (resistivity > 18 M $\Omega$  cm at 25 °C). Other chemicals were of HPLC or analytical grade provided by Panreac and Merck.

### 2.2. Real OOMW sample

The real OOMW was obtained from a decanter receiving wastewater generated upon cleaning stages during the premium extra virgin olive oil production at a small size oil mill in north-eastern Spain. It was collected in November of 2015 and kept at 4 °C before use. The treatments were made after filtration of the OOMW sample with an 18  $\mu\text{m}$  filter, spiking or not 1.03 mM 4-hydroxyphenylacetic acid, without or with dilution with Milli-Q water.

### 2.3. Electrolytic system

All the trials were carried out with an open, undivided, cylindrical glass cell containing 100 mL solutions under vigorous stirring with a magnetic bar at 700 rpm. The cell was surrounded with a double jacket where thermostated water was recirculated at 35 °C. This was the maximum temperature that could be used avoiding significant solvent evaporation. A 3 cm<sup>2</sup> BDD (deposited onto *p*-Si) electrode supplied by NeoCoat (La-Chaux-de-Fonds, Switzerland) was used as the anode and a 3 cm<sup>2</sup> carbon-PTFE air-diffusion electrode supplied by E-TEK (Somerset, NJ, USA) as the cathode. The interelectrode gap was about 1 cm. The cathode was mounted as reported elsewhere [27] and was fed with air pumped at 300 mL min<sup>-1</sup> for continuous H<sub>2</sub>O<sub>2</sub> generation on site. The experiments were performed at constant  $j$  provided by an EG&G Princeton Applied Research 273A potentiostat-galvanostat. The surfaces of the anode and cathode were initially cleaned and activated, respectively, under polarization in 100 mL of 0.050 M Na<sub>2</sub>SO<sub>4</sub> at 100 mA cm<sup>-2</sup> for 180 min.

Solutions with 0.21–2.06 mM 4-hydroxyphenylacetic acid and 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0 were comparatively treated by AO-H<sub>2</sub>O<sub>2</sub>, EF and PEF at  $j$  values between 16.7 and 100 mA cm<sup>-2</sup>. These EAOPs were also applied to degrade the filtrated OOMW sample at pH 3.0, either raw or diluted with ultrapure water, in the absence and presence of 1.03 mM 4-hydroxyphenylacetic acid. For EF and PEF, 0.50 mM Fe<sup>2+</sup> was added as Fenton's catalyst since it was found optimal for many organics degraded under similar conditions [36–39]. For PEF, a Philips TL/6W/08 fluorescent black light blue tube of  $\lambda_{\text{max}} = 360\text{ nm}$  placed at 8 cm above the solution surface was used. The average power density of this lamp was 5 W m<sup>-2</sup>, as determined with a Kipp&Zonen CUV 5 UV radiometer.

### 2.4. Analytical methods

The pH and conductance of synthetic sulfate solutions and real OOMW samples were measured with a Crison GLP 22 pH-meter and a Metrohm 644 conductometer, respectively. The turbidity was determined with a WTW TURB 55 IR turbidimeter. The chemical oxygen demand (COD) was measured with Hach Lange LCK014, LCK514 and LCK614 COD cuvette tests using a Hach DR 3900 UV-vis spectrophotometer. Other parameters of the OOMW were determined according to the Standard Methods [40]. The 5-day biochemical oxygen demand (BOD<sub>5</sub>) was obtained following a respirometric method with a WTW Oxitop 12 system using seed from a municipal wastewater treatment plant (method 5210 D). Total solids (TS) and total suspended solids (TSS) were determined upon evaporation and drying to constant weight in an oven at 103–105 °C (methods 2540 B and C). Phenol index was obtained according to the 4-aminoantipyrine direct spectrophotometric method 5530 D. Oil and grease content was measured via the

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