



Contents lists available at ScienceDirect

## Journal of Hazardous Materials

journal homepage: [www.elsevier.com/locate/jhazmat](http://www.elsevier.com/locate/jhazmat)



# Degradation of *trans*-ferulic acid in acidic aqueous medium by anodic oxidation, electro-Fenton and photoelectro-Fenton

Nelly Flores, Ignasi Sirés, José Antonio Garrido, Francesc Centellas, Rosa María Rodríguez, Pere Lluís Cabot, Enric Brillas\*

Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

### HIGHLIGHTS

- *trans*-Ferulic acid degradation by EAOPs using a stirred BDD/air-diffusion cell.
- Slow substrate abatement and poor mineralization by AO-H<sub>2</sub>O<sub>2</sub>.
- 98% Mineralization by PEF, but with rapid and similar substrate decay than by EF.
- Quicker degradation by SPEF due to the more potent photolytic action of sunlight.
- Reaction pathway with four primary aromatic products and three final carboxylic acids.

### ARTICLE INFO

#### Article history:

Received 11 October 2015

Received in revised form

19 November 2015

Accepted 20 November 2015

Available online xxx

#### Keywords:

Anodic oxidation

Electro-Fenton

Oxidation products

Photoelectro-Fenton

*trans*-Ferulic acid

### ABSTRACT

Solutions of pH 3.0 containing *trans*-ferulic acid, a phenolic compound in olive oil mill wastewater, have been comparatively degraded 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). Trials were performed with a BDD/air-diffusion cell, where oxidizing \*OH was produced from water discharge at the BDD anode and/or in the solution bulk from Fenton's reaction between cathodically generated H<sub>2</sub>O<sub>2</sub> and added catalytic Fe<sup>2+</sup>. The substrate was very slowly removed by AO-H<sub>2</sub>O<sub>2</sub>, whereas it was very rapidly abated by EF and PEF, at similar rate in both cases, due to its fast reaction with \*OH in the bulk. The AO-H<sub>2</sub>O<sub>2</sub> process yielded a slightly lower mineralization than EF, which promoted the accumulation of barely oxidizable products like Fe(III) complexes. In contrast, the fast photolysis of these latter species under irradiation with UVA light in PEF led to an almost total mineralization with 98% total organic carbon decay. The effect of current density and substrate concentration on the performance of all treatments was examined. Several solar PEF (SPEF) trials showed its viability for the treatment of wastewater containing *trans*-ferulic acid at larger scale. Four primary aromatic products were identified by GC-MS analysis of electrolyzed solutions, and final carboxylic acids like fumaric, acetic and oxalic were detected by ion-exclusion HPLC. A reaction sequence for *trans*-ferulic acid mineralization involving all the detected products is finally proposed.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The olive oil industry in Mediterranean countries like Spain, Italy, Greece and Portugal supplies about 77% of the worldwide output of this product. During the extraction of the olive oil, however, a volume of industrial effluents as large as 30 million cubic meters is produced annually in the world. Olive oil mill wastewater (OOMWW) has acidic pH near 5, high chemical and biochemical

oxygen demand up to 110 gL<sup>-1</sup> and 170 gL<sup>-1</sup>, respectively, and total solids contents up to 150 gL<sup>-1</sup> [1], which is very harmful for the environment by the negative effects over soil microbial population [2] and aquatic ecosystems [3]. Phenols, lipids, sugars and tannins are the main organic components of OOMWW, representing up to 37% of the total mass [4,5]. One of the most important phenolic compounds is *trans*-ferulic acid (4-hydroxy-3-methoxycinnamic acid), much more abundant than its *cis* isomer. *trans*-Ferulic acid is also present in the plant cell wall of various fruits and vegetables, possesses a high antioxidant activity and low toxicity after oral administration (LD<sub>50</sub> = 3200 mg kg<sup>-1</sup>) and has been detected in rivers, lakes and sea sediments [6]. At indus-

\* Corresponding author. Fax: +34 934021231.  
E-mail address: [brillas@ub.edu](mailto:brillas@ub.edu) (E. Brillas).

trial level, it is used as ingredient in many drug formulations and food additives, being its derivative vanillin of huge commercial importance in the food industry [7]. So far, little information about the degradation of *trans*-ferulic acid for wastewater treatment is available. Several authors have described its oxidation by pyrilium salt photosensitized with sunlight [8] and advanced oxidation processes (AOPs) such as catalytic wet oxidation [9], heterogeneous Fenton [10] and TiO<sub>2</sub> photocatalysis [11], but the use of powerful electrochemical AOPs (EAOPs) for treating water polluted with *trans*-ferulic acid has not yet been reported.

Over the last two decades, EAOPs have received growing attention for the remediation of wastewater contaminated with biorecalcitrant organics [12–16]. The common feature of these methods is the in situ generation of reactive oxygen species (ROS) such as hydroxyl radical ( $\bullet\text{OH}$ ), which can attack most organics up to their mineralization (conversion into CO<sub>2</sub> and inorganic ions) due to its high standard reduction potential ( $E^\circ = 2.80\text{ V/SHE}$ ). The most popular EAOP is anodic oxidation (AO), also so-called electrochemical oxidation. In AO, a high current density ( $j$ ) is usually applied to the anode M of the cell to produce oxidizing physisorbed hydroxyl radical M( $\bullet\text{OH}$ ) as intermediate of water discharge to O<sub>2</sub> at the anode surface by Reaction (1) [12,17–19]:

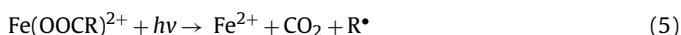


When considering the abatement of aromatic organics and even carboxylic acids, the physisorbed BDD( $\bullet\text{OH}$ ) generated at boron-doped diamond (BDD) anode has higher oxidation ability than M( $\bullet\text{OH}$ ) produced by other common anodes [20–23]. This is due to the larger O<sub>2</sub>-overpotential of BDD and the low interaction between its surface and  $\bullet\text{OH}$ , which favors its reaction with organics [12]. At present, the BDD electrode is the preferred anode for AO.

When an undivided cell is used with a carbonaceous cathode able to electrogenerate H<sub>2</sub>O<sub>2</sub>, the process is called AO-H<sub>2</sub>O<sub>2</sub>, where organics are preferentially destroyed by physisorbed M( $\bullet\text{OH}$ ) along with a minor participation of other ROS such as H<sub>2</sub>O<sub>2</sub> and its anodic oxidation product HO<sub>2</sub> $\bullet$  [13,14]. It is well-known that H<sub>2</sub>O<sub>2</sub> can be efficiently formed from the two-electron reduction of O<sub>2</sub> gas via reaction (2) at cathodes such as activated carbon fiber [24], carbon nanotubes [25,26], graphite felt [27], carbon modified with metals or metal oxides nanoparticles [28], carbon felt [29–31], carbon-polytetrafluoroethylene (PTFE) O<sub>2</sub> or air-diffusion [32–34], and BDD [35,36].



Another widely used EAOP is the electro-Fenton (EF) process, where a catalytic amount of Fe<sup>2+</sup> is added to the solution to enhance the oxidation power of H<sub>2</sub>O<sub>2</sub> via Fenton's Reaction (3) with production of Fe<sup>3+</sup> and  $\bullet\text{OH}$  in the bulk [29–34]. The optimum pH for EF is ~3 and organic pollutants are then destroyed by both kinds of ROS, M( $\bullet\text{OH}$ ) and  $\bullet\text{OH}$ . In our laboratory, we have been developing other EAOPs like UVA photoelectro-Fenton (PEF) or solar PEF (SPEF) in which the treated solution is irradiated with either artificial UVA light or sunlight, respectively [37–40]. This radiation causes the photoreduction of Fe(OH)<sup>2+</sup> species to Fe<sup>2+</sup> with  $\bullet\text{OH}$  generation via Reaction (4), as well as the photodecarboxylation of complexes of Fe(III) with generated carboxylic acids according to Reaction (5).



This paper presents a comparative study on the degradation of *trans*-ferulic acid solutions at pH 3.0 by AO-H<sub>2</sub>O<sub>2</sub>, EF and PEF using a stirred BDD/air-diffusion tank reactor. The mineralization process was also assessed by SPEF in order to check its potentiality at industrial scale. The effect of  $j$  and substrate concentration

on the performance of the EAOPs tested was examined to understand the role of the generated hydroxyl radicals and the action of UV light. The decay of *trans*-ferulic acid and the evolution of some products like vanillin and carboxylic acids were monitored by high-performance liquid chromatography (HPLC). Primary aromatic intermediates were identified by gas chromatography–mass spectrometry (GC–MS). Based on the results obtained, a plausible route for *trans*-ferulic acid mineralization by EAOPs is proposed.

## 2. Experimental

### 2.1. Chemicals

*trans*-Ferulic acid (99% purity) and vanillin (99% purity) were supplied by Sigma–Aldrich and used without further purification. Fumaric, acetic and oxalic acids were of analytical grade supplied by Merck. Heptahydrated Fe(II) sulfate and anhydrous sodium sulfate were of analytical grade supplied by Fluka. Analytical grade sulfuric acid purchased from Merck was used to adjust the initial solution pH to 3.0. All the solutions were prepared with high-purity water from a Millipore Milli-Q system (resistivity >18 M $\Omega$  cm at 25 °C). Other chemicals used for analysis were of HPLC or analytical grade provided by Avocado, Fluka and Merck.

### 2.2. Electrolytic systems

All the experiments were performed with an open, undivided, two-electrode cylindrical glass cell of 150 mL capacity. It was equipped with a double jacket for recirculating water at 35 °C by means of a Thermo Electron Corporation HAAKE DC 10 thermostat. This working temperature was chosen because it is the maximum value that can be used without significant water evaporation from the solution. All the assays were made under vigorous stirring with a magnetic bar at 700 rpm to ensure the transport of reactants toward/from the electrodes and homogenization. The electrodes were a BDD (deposited onto *p*-Si) anode purchased from NeoCoat (La-Chaux-de-Fonds, Switzerland) and a carbon-PTFE air-diffusion cathode purchased from E-TEK (Somerset, NJ, USA), both of 3 cm<sup>2</sup> geometric area and separated about 1 cm. The cathode was mounted as reported elsewhere [41] and was fed with air pumped at 300 mL min<sup>-1</sup> for H<sub>2</sub>O<sub>2</sub> generation from Reaction (2). The trials were carried out at constant  $j$  provided by an EG&G Princeton Applied Research 273A potentiostat-galvanostat.

Solutions of 100 mL containing *trans*-ferulic acid and 0.05 M Na<sub>2</sub>SO<sub>4</sub> as background electrolyte at pH 3.0 were comparatively treated by AO-H<sub>2</sub>O<sub>2</sub>, EF and PEF. In the two latter EAOPs, 0.50 mM Fe<sup>2+</sup> was added as catalyst since this content has been found optimal for many organics degraded under similar conditions [37–40]. For PEF, a Philips TL/6W/08 fluorescent black light blue tube of  $\lambda_{\text{max}} = 360\text{ nm}$  with average power density of 5 W m<sup>-2</sup>, determined with a Kipp & Zonen CUV 5 UV radiometer, was placed at 8 cm above the solution surface. Some experiments were also performed by SPEF upon direct exposition of the cell to sunlight irradiation in clear and sunny days of the summer 2015 in our laboratory of Barcelona (latitude: 41°23'N, longitude: 2°9'E). The average UV solar irradiation intensity from 300 to 400 nm was about 30 W m<sup>-2</sup>, as measured on the radiometer. Before starting the experiments, the surfaces of the anode and cathode were cleaned and activated, respectively, under polarization in 100 mL of a 0.05 M Na<sub>2</sub>SO<sub>4</sub> solution at 100 mA cm<sup>-2</sup> for 180 min.

### 2.3. Apparatus and analytical methods

The solution pH was measured on a Crison GLP 22 pH-meter. For total organic carbon (TOC) measurements, samples were withdrawn from treated solutions, filtered with 0.45  $\mu\text{m}$  PTFE filters

Download English Version:

<https://daneshyari.com/en/article/4980155>

Download Persian Version:

<https://daneshyari.com/article/4980155>

[Daneshyari.com](https://daneshyari.com)