

Ferulic acid treatment by electrochemical oxidation using a BDD anode



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ABSTRACT

The electrochemical oxidation of ferulic acid (FA) (4-hydroxy-3-methoxy-cinnamic acid), an important polyphenolic compound that can be found in olive oil mill wastewater, was studied by galvanostatic electrolysis using a plug-flow reactor equipped with a boron-doped diamond (BDD) anode and stainless steel cathode. The influence of several operating parameters, such as applied current, ferulic acid concentration, temperature, effect of the NaCl concentration and pH value, was investigated. HPLC, chemical oxygen demand and total organic carbon measurements were conducted to study the reaction kinetics of ferulic acid oxidation and mineralization. The specific energy consumption was also evaluated.

The experimental results showed that the anodic oxidation with BDD electrode was suitable for almost complete mineralization of 1 mM FA at 0.2 A in 210 min, due to the production of hydroxyl radicals on the BDD surface. The oxidation rate increased with applied current, while it was almost unaffected by temperature and pH value. Addition of NaCl to the solution favored the removal of FA due to mediation of active chlorine generated at the anode.

During electrolysis at pH 4, temperature of 20 °C and current of 0.2 A, 97% of COD was removed with a specific energy consumption of 9.5 kWh m⁻³.

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1. Introduction

The continuous growth of the olive oil industry increased the production of non-biodegradable waste known as olive mill wastewater (OMW). Due to its toxicity and inhibitor character to anaerobic digestion, OMW is one of the main environmental problems in Mediterranean countries in general, and particularly in certain areas of Spain, Italy, Turkey and Tunisia where there are many olive oil production plants. It is well known that the presence of phenolic compounds, such as sinapic acid, tyrosol, hydroxyphenol, ferulic, p-coumaric and caffeic acid, is the main responsible for the biorecalcitrant properties of OMW [1]. Since phenolic compounds are recalcitrant to conventional physicochemical and biological treatments [2,3], more efficient treatment of these effluents is necessary in order to reduce the impact of their discharge in the environment.

Recently advanced Oxidation Processes (AOPs) have been defined as effective processes for treatment of OMW or effluents containing phenolic compounds. These processes use hydroxyl radical, a powerful oxidizing agent, which is able to destruct target pollutants [4]. The oxidative degradation of polyphenol in aqueous media has been the

subject of several AOPs studies such as Fenton's reagent [5,6], ozonation [7], H₂O₂-mediated photodegradation [8], photo-Fenton [9] and electro-Fenton [10–12].

In this field, electrochemical methods can be a promising alternative to traditional processes for the treatment of phenolic compounds [13–22]. Many electrode materials have been studied for wastewater treatment, such as dimensionally stable anodes, noble metals (e.g. platinum) and carbon-based anodes, but the electrochemical oxidation of organics to CO₂ occurs with a significant rate and efficiency only using anodes with high oxygen evolution overpotential such as BDD [23–26]. Using these anodes working at high potential, reactive •OH are generated on their surface by water discharge, thus leading to overall combustion of organic compounds [27–32]:



Ferulic acid is a phenolic derivate of cinnamic acid and it is abundant in OMW [33]. Oxidation of ferulic acid (FA) was previously studied in literature [34, 35]. Thus, Beltran et al. [36, 37] studied the chemical oxidation of ferulic acid by Fenton's reagent or ozone and they calculated the kinetic rate constants. The performance of different catalysts during the catalytic wet oxidation of ferulic acid was

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investigated by Yadav and Garg [38], observing that the maximum COD and TOC removals (88% and 82%, respectively) were obtained using Cu/Ce/Activated Carbon catalyst. The electrochemical behavior of ferulic acid at gold and PbO₂ anode was studied by Trabelsi et al. [39] by cyclic voltammetry.

The goal of this paper is to present the result about the anodic oxidation of FA using a plug-flow reactor equipped with BDD electrode, under galvanostatic conditions. The impact of the main operating parameters, such as current density, pH, concentration, temperature and electrolyte, affecting COD, was investigated, in order to identify optimal experimental conditions.

2. Experimental

2.1. Chemicals

The synthetic solution was prepared dissolving different amount of ferulic acid (4-hydroxy-3-methoxy-cinnamic acid, C₁₀H₁₀O₄) in bidistilled water in 50 mM Na₂SO₄. Na₂SO₄ was chosen as the supporting electrolyte, because it does not generate some oxidizing species liable to react with organics and these ions, together with chlorides, nitrates and phosphates are commonly present in OMW. In some experiments different amounts of NaCl were also added to Na₂SO₄. H₂SO₄ and NaOH were used to adjust the pH of the solution. All the reagents used were analytical grade purchased by Carlo Erba Reagents. The molecular structure of the FA is given in Fig. 1.

2.2. Electrolytic system

The bulk electrolyses were performed in a one-compartment electrolytic flow cell with parallel plate electrodes applying a constant current in the range 0.2–1.5 A, using an AMEL 2055 potentiostat/galvanostat. BDD was used as the anode and stainless steel AISI 304 as the cathode. Both electrodes were circular with a geometric area of 50 cm² each and an interelectrode gap of 1 cm. The electrolyte was stored in a 0.35 L thermo regulated glass reservoir (20 °C) and circulated through the electrolytic cell by a centrifugal pump with a recirculation flow rate of 300 L h⁻¹.

The BDD thin-film electrode was supplied by Adamant Technologies (Neuchatel, Switzerland). It was synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single crystal p-type Si wafers. The temperature of the filament was in the range 2440–2560 °C and that of the substrate was about 830 °C. The reactive gas used was 1 ppm methane in dihydrogen containing 1 ppm of trimethylboron. The gas mixture was supplied to the reaction chamber with a flow rate of 5 L min⁻¹ giving a growth rate of 0.24 mm h⁻¹ for the diamond layer. The doping level of boron in the diamond layer expressed as B/C ratio was about 3500 ppm. The diamond film thickness obtained was about 1 μm, with a resistivity of 10–30 mΩ cm. In order to stabilize the electrode surface and to obtain reproducible results, the diamond electrode was pre-treated at 25 °C by anodic polarization in 1 mol L⁻¹ HClO₄ at 10 mA cm⁻² for 10 min using stainless steel as the counter electrode. This treatment made the surface hydrophilic.

2.3. Analysis

Evolution of FA concentrations during electrolyses was monitored by high performance liquid chromatography (HPLC) using a Thermo Spectra System P4000 chromatograph equipped with UV detector at 254 nm and fitted with a Altech C18 5 μm column (length 250 mm, i.d. 4.6 mm) at 25 °C. The analyses were carried out isocratically with a methanol/water 25:75 (v/v) mixture as mobile phase at a flow rate of 1 cm³ min⁻¹.

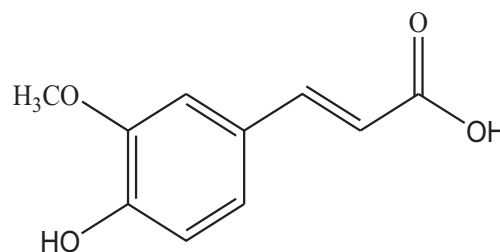


Fig. 1. Molecular structure of the ferulic acid.

The Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) of the initial and electrolyzed samples were determined with a Dr. Lange LASA50 system.

The current efficiency (CE) of the electrolysis, which was an average value, was calculated from the values of the COD using the relationship:

$$CE(\%) = \frac{COD_0 - COD_t}{8It} FV \times 100 \quad (3)$$

Where COD₀ and COD_t are the chemical oxygen demands at times t = 0 and t (in gO₂ L⁻¹), respectively, and I is the current (A), F is the Faraday constant (96487 C mol⁻¹), V is the volume of the electrolyte (L).

The specific energy consumption (E_c, in kWhm⁻³) was obtained as follows:

$$E_c = \frac{U_{cell}It}{V \cdot 3600} \quad (4)$$

Where U_{cell} is the average cell voltage (V), I is the current (A), t is the electrolysis time (s) and V is the volume of the treated solution (L).

3. Results and discussion

3.1. Degradation of ferulic acid

The decay of FA concentration during the anodic oxidation at 0.2 A was studied by reverse-phase HPLC, which displayed a well-defined peak at retention time t_R = 4.3 min as shown in Fig. S1 (Supporting Information). Fig. 2 shows that FA was completely removed on BDD anode in 180 min. It can be also seen that the concentration of FA decreases exponentially and its oxidation can be satisfactorily described by a pseudo-first order reaction kinetic (inset of Fig. 2). Apparent rate constants determined by plotting the Ln (FA₀/FA_t) against time was 0.019 min⁻¹, where FA₀ and FA_t are the concentration of FA at t = 0 and t.

However, the complete removal of FA does not mean that all the organic compounds present in the solution are completely removed because some oxidation reaction intermediates could be formed. Thus, the mineralization of FA was monitored measuring the TOC of the solution during the electrolysis of 1 mM FA solution at 0.2 A and the results are presented in Fig. 3. After 210 min of treatment TOC removal was almost complete, meaning that all the organic compounds (FA, its oxidation aromatic intermediates and carboxylic acids as organic by-products) are completely mineralized to CO₂ and water according to the reaction:



The faster decrease of FA concentration (measured by HPLC and expressed in term of mg L⁻¹ of carbon) compared to the removal of TOC revealed that some oxidation intermediates are formed during the electrolysis. The evolution of their concentration obtained by the difference between TOC and FA concentration, increased in the first 30 min and then it progressively decreased up to zero.

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