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Removal of 4-hydroxyphenylacetic acid from aqueous medium by electrochemical oxidation with a BDD anode: Mineralization, kinetics and oxidation products

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

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ABSTRACT

The degradation of 100 mL of solutions containing 4-hydroxyphenylacetic acid in 0.050 M Na_2SO_4 at pH 3.0 has been performed by anodic oxidation with electrogenerated H_2O_2 (AO-H_2O_2) using a stirred tank reactor equipped with a boron-doped diamond (BDD) anode and an air-diffusion cathode. An almost total mineralization with 95.5% total organic carbon (TOC) removal was achieved for a 1.03 mM substrate solution at 100 mA cm^{-2}. The effect of current density between 16.7 and 100 mA cm^{-2} and 4-hydroxyphenylacetic acid content between 0.21 and 2.06 mM was examined. Greater current efficiency with lower specific energy consumption and smaller mineralization was found at low current density and high substrate concentration. The TOC abatement as well as the 4-hydroxyphenylacetic acid concentration decay obeyed a pseudo-first-order kinetics. The oxidation role of hydroxyl radical formed from water discharge at the BDD anode is explained on the basis of its electrogeneration rate and competitive wasting reactions. 4-Hydroxybenzenemethanol and its derivative 4-hydroxybenzenealdehyde were identified as primary aromatic by-products by gas chromatography-mass spectrometry. Ion-exclusion HPLC allowed the detection of low amounts of the persistent oxalic acid during the AO-H_2O_2 process. The remaining TOC in final electrolyzed solutions is related to the presence of a large proportion of unidentified by-products that are even more recalcitrant than common short-chain aliphatic carboxylic acids.

1. Introduction

The olive oil production in Mediterranean countries such as Spain, Portugal, Greece and Italy accounts for near 77% of world output. The extraction of olive oil causes the annual release of >30 million cubic meters of industrial effluents worldwide. Olive oil mill wastewater (OOMW) has an acidic pH near 5 and is highly hazardous for the aquatic environment because it presents a chemical oxygen demand up to 110 g L^{-1}, a biochemical oxygen demand up to 170 g L^{-1} and total solids concentration up to 150 g L^{-1} [1,2]. The organic components of OOMW include phenols, lipids, sugars and tannins, related to up to 37% of its total mass [3,4]. Several authors have reported the treatment of these effluents by catalytic wet air oxidation [5] and electrochemical degradation with a Pt anode [6,7], which lead to a significant reduction of phenolic derivatives. In order to establish an optimum integral treatment of such wastewater, the degradation of its main single components has to be addressed. 4-Hydroxyphenylacetic acid is one of the most abundant phenolic components detected in OOMW, also found in beer. At industrial level, it is used as intermediate in the production of β-blockers like atenolol and other chemicals. It is a primary product upon oxidation of tyrosol (4-hydroxyphenylethanol), another phenolic compound in OOMW [8,9]. However, little information is available about the degradation of 4-hydroxyphenylacetic acid for wastewater treatment. Only its removal by several advanced oxidation processes (AOPs) such as zero-valent iron [10] and UV/H_2O_2 and Fenton's reagent [11] has been described, but the use of powerful electrochemical AOPs (EAOPs) for treating wastewater contaminated with 4-hydroxyphenylacetic acid has not been reported yet.

EAOPs are environment-friendly technologies that operate at mild conditions without addition of noxious chemicals since the main oxidant is produced by the electron [12–15]. The great oxidation power of these methods to destroy the organic matter in wastewater is related to the continuous in situ production of reactive oxygen species (ROS), pre-eminently the powerful hydroxyl radical (•OH). This species, the second strongest oxidant known after fluorine, possesses such a high standard reduction potential ($E°$(•OH/H_2O) = 2.80 V/SHE) that can non-selectively react with most organics via dehydrogenation and/or hydroxylation up to their mineralization (conversion into CO_2, water and inorganic ions) [13]. Anodic oxidation (AO), also called electrochemical oxidation, is the most popular EAOP. In this procedure, a solution with organic pollutants is placed in the electrolytic cell to be oxidized either by direct charge transfer at the anode M or, if a high current is applied, by adsorbed hydroxyl radical M(•OH) formed as

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* Corresponding authors.
E-mail addresses: i.sires@ub.edu (I. Sirés), brillas@ub.edu (E. Brillas).

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intermediate of O_2 evolution from water oxidation [13,16,17]. The oxidation ability of AO depends on the selected anode. It has been found that the most potent one is the boron-doped diamond (BDD) thin-film electrode in which the physisorbed BDD(•OH) is produced from the following reaction [16,18,19]:

$$\text{BDD} + H_2O \rightarrow \text{BDD}(\bullet\text{OH}) + H^+ + e^- \quad (1)$$

The use of the BDD anode presents important technological advantages such as remarkable corrosion stability in harsh media, inert surface with low adsorption of BDD(•OH) and organics and a greater O_2-evolution overvoltage than other anodes. These characteristics significantly upgrade the removal of organic pollutants by hydroxyl radicals [13,16], allowing the mineralization of aromatics [14,18,20–29] and by-products like aliphatic carboxylic acids [30], with much higher oxidation ability than traditional anodes like Pt [31–33] and PbO_2 [34].

An alternative to raw AO relies on its combination with electrogenerated H_2O_2, so-called AO-H_2O_2. In this procedure, H_2O_2 is continuously produced by the two-electron cathodic reduction of injected pure O_2 or air via reaction (2) [12,13]:

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \quad (2)$$

Effective cathodes for reaction (2) include carbonaceous materials like BDD [35], activated carbon fiber [36], carbon nanotubes [37], carbon sponge [38], carbon felt [39–41] and carbon-polytetrafluoroethylene (PTFE) gas diffusion composites [14,15,42,43].

AO-H_2O_2 has been developed in our laboratory using a gas-diffusion cathode [12,43], which minimizes the possible cathodic reduction of organics because of the very efficient supply of H_2O_2 to the medium from reaction (2). We have found that the concentration of this species attains a quasi-steady state once its electrogeneration and removal rates equate. H_2O_2 is mainly destroyed upon oxidation to O_2 at the BDD anode, thus forming hydroperoxyl radical from reaction (3). Therefore, in AO-H_2O_2, organic pollutants can be removed by BDD(•OH) and, to much smaller extent, by other weaker oxidants like H_2O_2 and BDD(HO_2•).

$$\text{BDD} + H_2O_2 \rightarrow \text{BDD}(HO_2\bullet) + H^+ + e^- \quad (3)$$

This paper reports a study on the degradation of acidic solutions of 4-hydroxyphenylacetic acid by AO-H_2O_2 using a BDD/air-diffusion tank reactor. The influence of current density (j) and substrate content on degradation rate, mineralization current efficiency (MCE) and energy consumption was examined. The decay kinetics of 4-hydroxyphenylacetic and the evolution of generated carboxylic acids were monitored by high-performance liquid chromatography (HPLC). The degradation process was ascertained by identifying the products using gas chromatography-mass spectrometry (GC-MS).

2. Experimental

2.1. Chemicals

4-Hydroxyphenylacetic acid (98% purity) was purchased from Sigma-Aldrich and used as received. Analytical grade oxalic acid and anhydrous Na_2SO_4 were supplied by Merck and Fluka, respectively. Analytical grade H_2SO_4 purchased from Acros Organics was used to adjust the initial pH to 3.0. All the aqueous solutions were prepared with ultrapure water from a Millipore Milli-Q system (resistivity >18 MΩ cm at 25 °C). Other chemicals used for analysis were of HPLC or analytical grade provided by Panreac and Merck.

2.2. Electrolytic System

All the trials were carried out in an open, undivided, cylindrical glass cell containing 100 mL solutions. The cell was surrounded with a double jacket where water was recirculated at 35 °C regulated by a Thermo Electron Corporation HAAKE DC 10 thermostat. This temperature was the maximum value that could be used to avoid significant solvent evaporation. All the assays were performed under vigorous stirring with a magnetic bar at 700 rpm for homogenization and for ensuring maximum mass transport of reactants toward/from the electrodes. A 3 cm^2 BDD (deposited onto *p*-Si) electrode supplied by NeoCoat (La-Chaux-de-Fonds, Switzerland) was used as the anode and a 3 cm^2 carbon-PTFE air-diffusion electrode supplied by E-TEK (Somerset, NJ, USA) was used as the cathode. The interelectrode gap was about 1 cm. The cathode was mounted as reported elsewhere [42] and was fed with air pumped at 300 mL min^{-1} for continuous H_2O_2 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_2SO_4 at 100 mA cm^{-2} for 180 min. Aqueous solutions with 0.21–2.06 mM 4-hydroxyphenylacetic acid and 0.050 M Na_2SO_4 at pH 3.0 were treated by AO-H_2O_2 at j values between 16.7 and 100 mA cm^{-2}.

2.3. Analytical Methods

The solution pH was measured with a Crison GLP 22 pH-meter. For total organic carbon (TOC) determinations, samples were withdrawn from treated solutions, filtered with 0.45 μm PTFE filters from Whatman and directly injected into a Shimadzu VCSN TOC analyzer. Reproducible values with ±1% accuracy were always found.

Assuming the following total mineralization for 4-hydroxyphenylacetic acid:

$$C_8H_8O_3 + 13\,H_2O \rightarrow 8\,CO_2 + 34\,H^+ + 34\,e^-. \quad (4)$$

the MCE values for each trial were estimated as follows [26,29]:

$$\text{MCE}(\%) = \frac{n\ FV\Delta(\text{TOC})_{exp}}{4.32 \times 10^7 m\ I\ t} \times 100 \quad (5)$$

where $n = 34$ is the number of electrons for the mineralization process, as shown in Eq. (4), F is the Faraday constant (96,487 C mol^{-1}), V is the solution volume (L), $\Delta(\text{TOC})_{\text{exp.}}$ is the experimental TOC decay (mg C L^{-1}), 4.32×10^7 is a conversion factor to homogenize the units (3600 s h^{-1} × 12,000 mg C mol^{-1}), $m = 8$ is the number of carbon atoms of 4-hydroxyphenylacetic acid, I is the applied current (A) and t is the electrolysis time (h).

The specific energy consumption per unit TOC mass (EC_{TOC}) was estimated from Eq. (6) [29,43]:

$$EC_{TOC}\left(\text{kWh}(\text{gTOC})^{-1}\right) = \frac{E_{\text{cell}}It}{V\Delta(\text{TOC})_{\text{exp}}} \quad (6)$$

where E_{cell} is the average cell voltage (in V) and the rest of parameters have been defined above.

The 4-hydroxyphenylacetic acid abatement was followed by reversed-phase HPLC using a Waters 600 LC fitted with a BDS Hypersil C18 6 μm, 250 mm × 4.6 mm, column at 35 °C and coupled to a Waters 996 photodiode array detector selected at $\lambda = 277.0$ nm. Measurements were made by injecting 10 μL aliquots into the LC and eluting an acetonitrile/water (60:40) mixture at 0.6 mL min^{-1} as mobile phase. The chromatograms exhibited a well-defined peak at retention time (t_r) of 5.0 min. Generated carboxylic acids were identified by ion-exclusion HPLC using the same LC fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm, column at 35 °C and the photodiode array detector selected at $\lambda = 210.0$ nm. Aliquots of 10 μL were also injected into the LC and the mobile phase was 4 mM H_2SO_4 at 0.6 mL min^{-1}. The chromatograms displayed a well-defined peak related to oxalic acid at $t_r = 7.0$ min.

The organic products generated upon treatment of 1.03 mM 4-hydroxyphenylacetic acid solutions at 30 and 90 min of AO-H_2O_2 at 33.3 mA cm^{-2} were identified by GC-MS using a NIST05-MS library to

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