Recovery of hydroxytyrosol a high added value compound through tyrosol conversion by electro-Fenton process

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ABSTRACT

The electrochemical oxidation of tyrosol (TY) in aqueous solutions has been studied in order to convert it into hydroxytyrosol (HTY) which is well known for its potentially high added value. This reaction was performed by the electro-Fenton (EF) process using a carbon fiber cloth as cathode and Pt anode. The evolution of the concentrations of TY and its oxidation products HTY and hyroquinone (HQ) during electrolysis, was monitored by means of high performance liquid chromatography (HPLC). The experimental data indicated that the rate of TY disappearance follows a pseudo first order kinetic. The HTY maximum concentration obtained during electrolysis increases with the initial TY concentration. While, it decreases when the applied current increases. The preponderance of HTY with respect to HQ was explained by its stabilization by complexation with iron ions. Finally, a mechanistic pathway for the TY oxidation by the EF process was proposed.

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1. Introduction

The HTY (3,4 dihydroxyphenylethanol) is one of the main phenolic components of olive oil. It is present in the fruit and olive leaf. It has been well documented that this phenolic compound possesses antioxidant properties, antimicrobial actions, antiinflammatory activities and beneficial effects on the cardiovascular system while preventing oxidative stress situations [1]. HYT also exerts a neuroprotective effect. A modeling study in vitro Parkinson's disease has shown that the HTY significantly protects neurons against molecules inducing their degradation, and thus against the dead neuronale [2]. Therefore, larger amounts of this compound are required at competitive prices, so that it can be used, for instance, as a preservative element in foods.

The production of HTY has been the subject of various works including chemical [3–6], and enzymatic [7] synthetic process. It has been shown that HTY could be produced with high yield and purity from 3,4-dihydroxyphenylacetic by the action of various reductants such as sodium borohydride [3], lithium aluminium hydride [4,5] and tetrabutylammonium borohydride [6]. However, the used procedures are complex and involve the use of hazardous and expensive reagents like the said reductants, trimethylsilyldiazomethane, hydrochloric acid and toxic solvents such as

chloroform, hexan and ethyl acetate. Furthermore, HTY can be enzymatically obtained with good yield, by the intermediary of its oxidized form using mushroom tyrosinase. Hence the need of the reducing action of the used ascorbic acid [7]. Moreover, HTY could be isolated by chromatographic methods of purification from oilve oil mill waste waters [8] and olive leaves [9]. But, the purification methods are generally characterized by their lengthy procedures, their consumption of large amounts of energy and solvents, and their low extraction yields. Additionally, organic solvents can be quite harmful to the environment and human health.

In our previous works we have investigated the electrochemical conversion of organic compounds toward a high added value compounds [10–14]. These studies concern the electrochemical production of o-tolualdehyde, p-tolualdehyde [10] and 2,6-dimethyl-1,4-benzoquinone [11] from respectively o-, p- and m-xylenes oxidation by the intermediary of the Ce^{4+}/C^{3+} redox couple, chlorotrifluoroethylene from trichloro-1,1,2-trifluoroéthane reduction by the intermediary of NH_4^+/NH_4 redox couple [12], 3-O-methylgallic acid from syringic acid oxidation [13] and 3,4-dihydroxyphenylacetic acid from phenylacetic acid oxidation [14]. The present work aims to examine the conversion of TY into HTY by electro-Fenton (EF) process using a carbon fibers cloth cathode. Carbon fibers are an attractive material for cathodic H_2O_2 generation thanks to their high catalytic activity for oxygen reduction and high overpotential for hydrogen evolution.
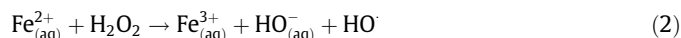
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Moreover they are commercially availables and have high chemical resistance, high conductivity and high surface area [15,16].

Furthermore, it should be noted that contrary to HTY, TY is commercially available. Moreover, the latter has weaker antioxidant activity compared to that of HTY due to its lack of orthodiphenolic structure [17]. In a previous study, the electrochemical oxidation of TY by EF using the pyrite as catalyst and a felt carbon as cathode has been examined but the objective was its complete incineration [18].

The EF process was well described and considered as an emerging technology for oxidizing organic compounds [19]. The performance of this process is based on the electrochemical in situ generation of H_2O_2 from the continuous aeration on the cathode (Eq. (1)). The Fe^{2+} present in the electrolyte, catalyses the generation of homogeneous hydroxyl radicals from H_2O_2 (Eq. (2)). Furthermore, Fe^{2+} is continuously recycled by its cathodic reduction as showing by (Eq. (3)). The secondary reaction of hydrogen evolution (Eq. (4)) can be triggered at relatively high cathodic currents.

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$Fe^{2+}_{(aq)} + H_2O_2 \rightarrow Fe^{3+}_{(aq)} + HO^-_{(aq)} + HO^{\cdot} \tag{2}$$

$$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)} \tag{3}$$

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2HO^-_{(aq)} \tag{4}$$

However, a part of hydroxyl radicals can be lost by the following parasitic reactions:

$$2HO^{\cdot} \rightarrow 1/2 O_2 + H_2O \tag{5}$$

$$Fe^{2+}_{(aq)} + HO^{\cdot}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + HO^-_{(aq)} \tag{6}$$
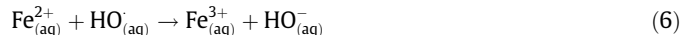
According to its non-selectivity oxidation action, the EF process has been thoroughly and successfully applied to the mineralization of toxic and persistent organic pollutants [20–22].

2. Materials and methods

2.1. Chemicals

TY (98%) was purchased from Alfa Aesar Company. Pure HTY was provided by SEPROX BIOTECH, S.L., (Madrid, Spain). Na_2SO_4 and $FeSO_4 \cdot 7H_2O$ were purchased from Chemi-Pharma and Acros. Acetonitrile (HPLC grade) was purchased from PANREAC.

All solutions were prepared with ultrapure water obtained from Millipore Simplicity 185 system (conductivity $<6 \cdot 10^{-8}$ S cm^{-1} at 25 °C). The pH of solutions was adjusted using analytical grade sulfuric acid (Scharlau).

2.2. Electrochemical cell

The electrolysis of TY solutions were carried out in an galvanostatic regime under magnetic stirring using a DC power supply (model ATTEN TPR 3303-3C-LG precision Co. Ltd, Korea). The electrolytic cell is an undivided Pyrex glass thermoregulated at 30 ± 0.5 °C. The cathode was a carbon fibers cloth (l = 5 cm, Ø = 3.5 cm). The anode was a cylindrical Pt grid (l = 4.5 cm, Ø = 5 cm) surrounding the cathode. The electrolytic solutions (Vs = 130 mL) initially contained TY with Na_2SO_4 at 50 mmol L^{-1} as background electrolyte and ($Fe (SO_4) \cdot 7H_2O$) as catalyst at the same concentration used in a previous work (1 mmol L^{-1}) [23]. The solution pH was adjusted at 3.0 using sulfuric acid. This value of pH was selected as the optimum one to carry out Fenton's reaction (Eq. (2)), according to the literature data on the EF process

[24]. Compressed pure oxygen was bubbled through the solution for 10 min, prior to the electrolysis to saturate the aqueous solution in oxygen, in order to continuously generate H_2O_2 from the electro-reduction of dissolved O_2 according to Eq. (1).

2.3. Analysis procedures

TY and all other aromatics were identified and quantified by high performance liquid chromatography (HPLC) using a Perkin Elmer Series 200 chromatograph. This latter is equipped with a dual pump and Waters Spherisorb C18 column (150mm × 4.6 mm) coupled with a UV–VIS detector. The mobile phase was acetonitrile and water mixtures. The volumic percentage of acetonitrile varied linearly with time as follows: from 10 to 25% for the first 25 min, then from 25 to 80% up to 35 min, after isocratic for 2 min, from 80 to 100% up to 43 min and then back to 10% up to 46 min. The flow rate was 0.6 mL min^{-1} and the injection volume was 20 μL and the UV–VIS detector was set at λ = 280 nm.

3. Results and discussion

Firstly, the electrolysis of 12.5 mmol L^{-1} TY aqueous solution was carried out using the EF process at 100 mA. Fig. 1A shows the chromatogram of the electrolyte recorded after 4 h of electrolysis.
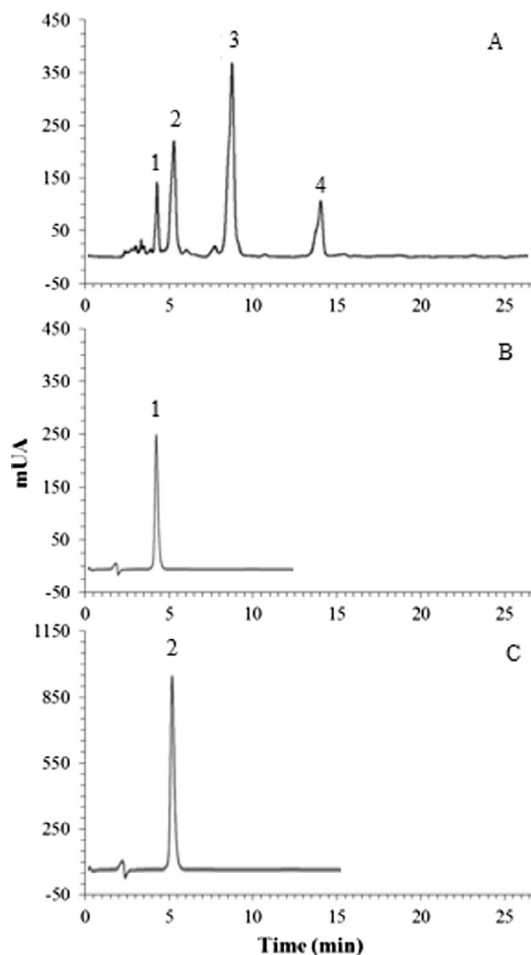

Fig. 1. HPLC chromatograms of: (**A**) TY oxidation by EF process after 4 h electrolysis. [TY]$_0$ = 12.5 mmol L^{-1}; I = 100 mA; T = 30 C°. Peaks: (1) HQ, (2) HTY; (3) TY, (4) Oligomere; (**B**) HQ standard; (**C**) HTY standard.